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THREE ADDITIONS TO THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN.

THE Kohlrausch-Ostwald method for determining the electrical conductivity of electrolytes by means of an alternating current and telephone is very accurate and easy to use so long as the induction coil gives a clear high note. This condition, however, is not easy to fulfil, for, owing to the magnetization of the steel spring current breaker, the adjustment is soon lost. This objection holds for all coils which use steel for the vibrator whether in the form of a spring or wire. In preparing four sets of apparatus for conductivity so much difficulty was experienced in adjusting the coils that it was decided to find, if possible, another form of interruptor which would be free from this objection. As a result of this search an attachment was found which not only gives a clear high note, and allows of rapid adjustment, but which can be used for one set or for a number of sets of apparatus so that in the latter case all may be adjusted by one operation. Each piece of apparatus is

set up as usual except that the current breaker is removed from
each coil, the interrupting being done for all in another room by
an apparatus run by another source of electricity. This
apparatus is a modified form of Professor M. I. Pupin's electro-
dynamic interruptor. The modifications referred to consist in
the use of an electromagnet instead of the somewhat uncommon
Weston permanent one, and in the interruption of a separate
circuit instead of that which causes the string to vibrate. A
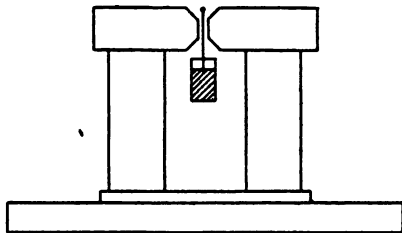
Fig. 1.

horseshoe electromagnet with special pole pieces (Fig. 1) is
mounted vertically upon a base-board. On these pole pieces is
fastened an oblong framework of brass, on the ends of which are
screw devices to which the ends of a brass wire may be soldered
and kept at any desired tension, between the pole pieces. Two
mercury cups are placed the one in front and the other behind
the magnet into each of which dips a short piece of amalgamated
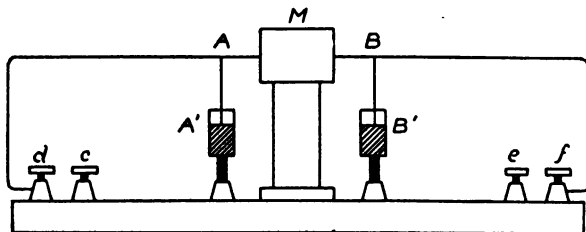
Fig. 2.—*c* is connected to B' and *e* to A' underneath the base. The
current enters at *d* and *c* and one portion goes to the electro-
magnet M by wires not shown in the figure.

copper wire which is soldered to the brass wire. These mercury
cups are so arranged upon screws that they may be raised or
lowered so as to be in contact with the copper dippers. Fig. 2
shows the arrangement of the wire, cups and magnet with their
connections. The current (three to six volts, taken from the

electric light circuit or from storage cells) enters at the two
binding-posts c and d and divides one portion going to the
magnet through wires not shown in the figure, the other going
from c through the wire to B, to the mercury at B' and back to d.
When the current is flowing in this way, the wire is repelled by
the magnet so that the contact at B' is broken but made again in-
stantaneously by the tension of the wire.   In this way the wire is
retained in rapid vibration, and, if the cup A is properly adjusted,
any battery circuit connected through e, A', A, and f will be inter-
rupted.   By connecting a Leclanché cell with an induction coil
(with the breaker removed) through the two binding-posts e and f
a rapidly alternating current is obtained and a clear high adjustable
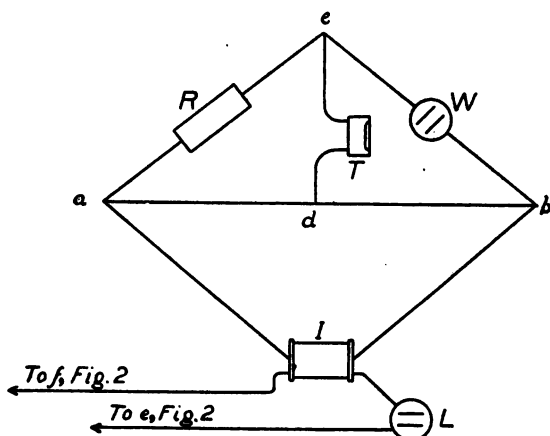
Fig. 3.—R is the known resistance, W the electrolytic cell, I the
coil, L the Leclanché cell and T the telephone.

note produced in the telephone. Fig. 3 shows the connections for a
piece of apparatus set up in the way described so that no further
explanation is necessary.   Naturally any number of sets may be
connected in this way through the interruptor, the same tone
being obtained in all, and all may be adjusted at once.   If the
current necessary for the operation of the vibrator were not so
great only one mercury cup would be necessary, but it has been
found more satisfactory to simply interrupt the current from a
single cell and thus to avoid heating and polarization effects at
the electrodes.   The arrangement described has been in use in

this laboratory for more than a year and has given great satisfaction.[1]

The second addition is designed for use in determining the conductivity of water or other substances of high resistance. In such cases in using the simple Ostwald form of bridge, the reading is very near one end so that the possible error, due to bad end contact, is very large. The arrangement proposed lengthens the bridge, only the one small portion represented by the one meter of wire being used, and so all readings are multiplied by a certain factor, and caused to approach the middle of the wire where the results are most accurate. This end is reached by placing certain lengths of insulated bridge wire on spools between the actual bridge wire and the arm of the bridge (between *b* and *W* Fig. 3). Spools containing four, nine, and nineteen meters of the bridge are prepared so that by inserting these, with mercury contacts, the readings are multiplied by five, ten, and twenty, respectively, that spool being used which brings the reading nearest the middle of the bridge. The idea is employed in the more elaborate bridges used by physicists, and also in the simple Ostwald form for the determination of electromotive force[2] but, so far as I know, it has never been used for conductivity. Its results, however, are very satisfactory and the idea is recommended to others.

The third addition proposed is for the purpose of ascertaining, as quickly and accurately as possible, that point on the bridge which gives the minimum tone in the telephone. The regular method of determining this point is first to locate it approximately and then to fix it by finding two points, one on either side of it, at which the tone has the same intensity. When these two points have been found the reading midway between them gives the minimum. In using this method it is hard to match the two tones since it takes an appreciable time to move the sliding contact. If the two tones could follow one another immediately it would be very much simpler. To do this the block of wood which is used as the holder for the sliding contact is provided with two press keys instead of one, both being connected by the same binding-post. The contact points of these two press keys should be

either one-half or one centimeter apart and have vulcanite knobs upon which to rest the fingers. As soon as the approximate reading is found with one key the block is moved until both keys when pressed give a tone of the same intensity; the middle point is then the true minimum. It is well to have the one key movable so that the distance between the contacts may be reduced as the point is reached. By the use of this arrangement it is possible to find the point within a small fraction of a millimeter and much less experience is necessary for accurate results than by the ordinary process.

ON THE SURFACE-TENSIONS OF MIXTURES OF SUL-PHURIC ACID AND WATER, AND THE MOLECU-LAR MASS OF SULPHURIC ACID.

BY C. E. LINEBARGER.

THE apparatus employed in making the measurements of the surface-tension was that described in a previous number of this Journal.[1]

The sulphuric acid used was Baker and Adamson's "chemically pure" (sp. gr. 1.84), and was found on analysis to contain 4.98 per cent. of water. This acid was mixed in varying proportions with water and the mixtures analyzed. The specific gravities of some of the mixtures were determined, but most of them were taken from Lunge and Isler's tables[2] and the corrections 'for temperature applied by means of the data given by Bineau.[3]

The thermostat consisted of a beaker filled with water and provided with a stirrer. A layer of heavy oil was poured over the water so as to prevent evaporation. Readings were taken (never less than three at the same temperature) at intervals of about 5°. These were plotted and a smoothed curve (which was approximately a straight line) drawn through them. From this curve, readings were taken at temperature-intervals of 10°, and these were used in calculating the surface-tensions.

Readings were taken in the same way with pure water, from which with the aid of Ramsay and Shields' data[4] on the surface-

1 This Journal, 18, 514 (1896).
2 Ztschr. angew. Chem., 129 (1890). Landolt and Börnstein, 196.
3 Ann. chim. phys. (3), 26, 123 (1849).
4 Ztschr. phys. Chem., 12, 433 (1893).

tension of water at various temperatures, the values of the
"apparatus constant" were calculated for every 10°. These
were found to change slightly but regularly.

The numerical results of the determinations are given in the
following table and are represented graphically in Figs. I and II.
Curves for 0°, 20° and 50° only are drawn in Fig. I so as not
to crowd too much. As it is, the right-hand parts of the curves
practically coincide.

SURFACE-TENSIONS OF MIXTURES OF SULPHURIC ACID AND WATER.

2.65 per cent. H_2SO_4.

Tempera-ture.	Apparatus constant.	Distance between ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
0°	1.260	56.39	1.021	73.60
10°	1.266	55.71	1.019	72.69
20°	1.273	54.83	1.017	72.02
30°	1.278	54.04	1.015	71.13
40°	1.283	53.12	1.013	70.07
50°	1.290	52.13	1.011	69.01

5.16 per cent. H_2SO_4.

0°	1.260	55.83	1.037	74.02
10°	1.266	55.01	1.035	73.14
20°	1.273	54.18	1.033	72.31
30°	1.278	53.31	1.031	71.29
40°	1.283	52.43	1.029	70.43
50°	1.290	51.54	1.027	69.33

11.87 per cent. H_2SO_4

0°	1.260	54.02	1.081	74.75
10°	1.266	53.46	1.078	74.10
20°	1.273	52.86	1.075	73.48
30°	1.278	52.15	1.072	72.58
40°	1.283	51.32	1.069	71.52
50°	1.290	50.41	1.066	70.45

18.33 per cent. H_2SO_4.

0°	1.260	51.61	1.138	75.30
10°	1.266	51.00	1.133	74.44
20°	1.273	50.37	1.128	73.59
30°	1.278	49.72	1.125	72.75
40°	1.283	49.05	1.123	71.92
50°	1.290	48.30	1.118	70.90
60°	1.296	47.64	1.113	69.95
70°	1.303	46.87	1.108	68.89

35.13 per cent. H_2SO_4.

Tempera-ture.	Apparatus constant.	Distance be-tween ends of tubes in 0.025 inch.	Specific gravity.	Surface tension in dynes per cm.
0°	1.260	47.03	1.275	77.19
10°	1.266	46.75	1.268	76.68
20°	1.273	46.41	1.262	76.34
30°	1.278	46.05	1.255	75.45
40°	1.283	45.67	1.248	74.68
50°	1.290	45.26	1.242	74.05
60°	1.296	44.76	1.235	73.15
70°	1.303	44.22	1.228	72.25

58.05 per cent. H_2SO_4.

0°	1.260	40.03	1.494	77.60
10°	1.266	39.98	1.486	77.44
20°	1.273	39.95	1.478	77.25
30°	1.278	39.88	1.470	77.08
40°	1.283	39.78	1.462	76.76
50°	1.290	39.66	1.454	76.49
60°	1.296	39.46	1.446	76.03
70°	1.303	39.22	1.438	75.55

65.27 per cent. H_2SO_4.

0°	1.260	37.75	1.575	77.41
10°	1.266	37.74	1.567	77.34
20°	1.723	37.72	1.559	77.29
30°	1.278	37.70	1.531	77.13
40°	1.283	37.68	1.543	76.99
50°	1.290	37.65	1.535	76.89
60°	1.296	37.61	1.527	76.74
70°	1.303	37.40	1.519	76.31

80.45 per cent. H_2SO_4.

0°	1.260	28.84	1.752	66.60
10°	1.266	28.78	1.743	66.40
20°	1.273	28.65	1.734	66.32
30°	1.278	28.60	1.725	66.00
40°	1.283	28.56	1.716	65.92
50°	1.290	28.55	1.707	65.79
60°	1.296	28.50	1.698	65.67
70°	1.303	28.48	1.689	65.50

83.23 per cent. H_2SO_4.

0°	1.260	27.11	1.783	64.18
10°	1.266	27.09	1.774	64.09
20°	1.273	27.06	1.764	63.89

C. E. LINEBARGER.

Tempera- ture.	Apparatus constant.	Distance be- tween ends of tubes in 0.025 inch.	Specific Gravity.	Surface tension in dynes per cm.
30°	1.278	27.02	1.755	63.70
40°	1.283	27.00	1.746	63.54
50°	1.290	26.99	1.737	63.48
60°	1.296	26.97	1.728	63.37
70°	1.303	26.96	1.718	63.19

95.02 per cent. H_2SO_4.

0°	1.260	23.63	1.843	58.26
10°	1.266	23.54	1.833	57.97
20°	1.273	23.46	1.824	57.76
30°	1.278	23.40	1.814	57.53
40°	1.283	23.39	1.805	57.43
50°	1.290	23.36	1.796	57.36
60°	1.296	23.31	1.786	57.28
70°	1.303	23.24	1.775	56.89

The foregoing data show that both the addition of water to sulphuric acid and of sulphuric acid to water increases the surface-tension of the liquids. The increase in the surface-tension of the acid even when but a small proportion of water is mixed with it is especially marked. The maximum surface-tension is observed when about equal quantities of the two liquids are mixed. It is also shown that certain mixtures of sulphuric acid and water, although of different percentage composition, may yet have equal surface-tensions. This is clearly brought out in the curves for mixtures containing 58.05 per cent. and 65.27 per cent., respectively, of the acid; the curves cross at an abscissa-value of about 22°. Besides this observed instance, other mixtures have a similar behavior. The limits of the values of their composition and surface-tensions may be learned by an inspection of the figures.

A noteworthy peculiarity of strong solutions of sulphuric acid in water is the slight influence that changes of temperature have upon their surface-tensions. The curves in Fig. 2 become more and more horizontal the greater the percentage of acid in the mixtures. From these low values found for the temperature coefficients, certain conclusions may be drawn as to the degree of molecular polymerization of pure sulphuric acid. It is true that no determinations were made of the surface-tension of the pure acid, but it seems reasonable to conclude that the regularity of

the curves would extend to the abcissa-value of the pure acid.
Yet it is scarcely to be expected that anything like correct values
for the surface-tension of the pure acid would be obtained by
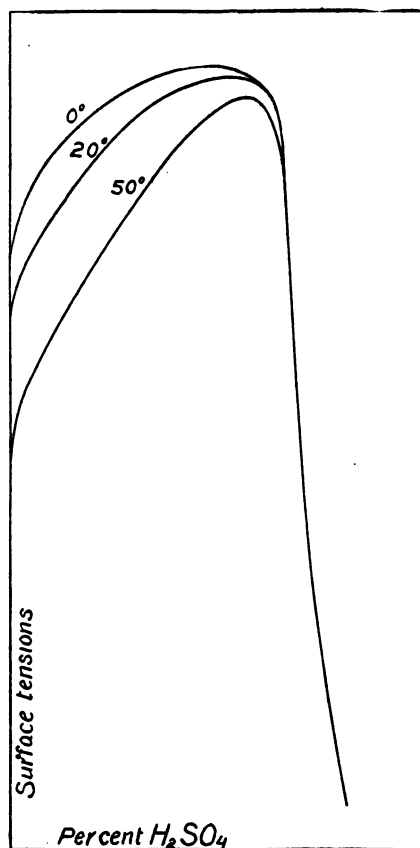
Fig. 1.

extrapolation, for the curves are too steep and close together.
All that is legitimate to infer is that the pure acid has a small
temperature coefficient with respect to its surface-tension.

Now according to the views of Ramsay and Shields[1] the
degree of polymerization of a liquid may be estimated by means
of the change of its molecular surface energy with the tempera-
ture. The smaller this is, the greater is the degree of polymeri-

1 *Loc. cit.*

zation of a liquid's molecules. The small temperature coefficient of sulphuric acid points then to a high degree of polymerization; the molecular mass of its molecule must be several times 98, the molecular mass corresponding to the formula H_2SO_4. Ramsay

58.05
65.27
35.13
11.87
5.16
2.65
18.33
80.45
83.23

Surface tensions

Temperature

95.02
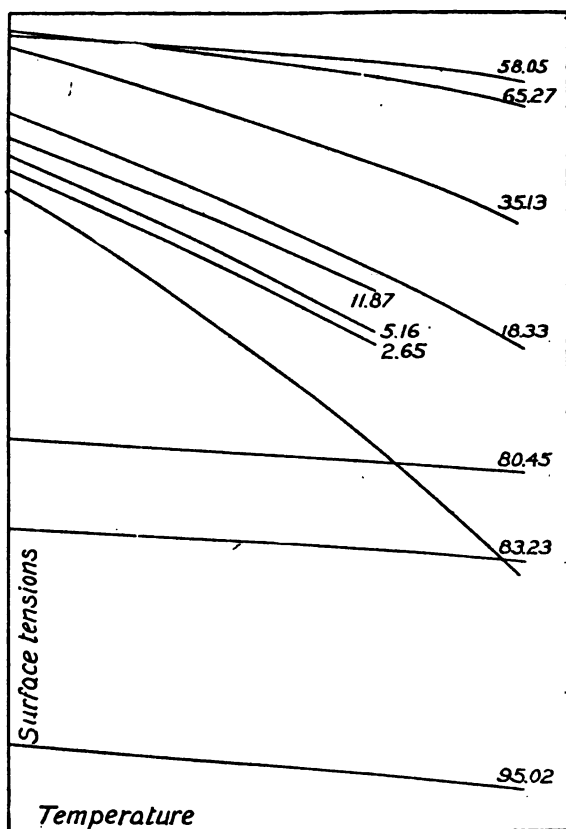
|Fig. 2.

in a lecture before the Chemical Society of Paris[1] stated that he had found it probable that the molecule of sulphuric acid could be approximately represented by the formula $(H_2SO_4)_{22}$. If this be true, sulphuric acid has the most complex molecule of any liquid as yet examined in that regard, and this complexity of

[1] This was printed in the *Revue Scientifique* (4), 2, 1 (1894). No data or details seem to have been given in any of the journals devoted to the publication of chemical research.

molecular structure may account for many of the anomalous properties of mixtures of sulphuric acid and water.

The conclusion that sulphuric acid is molecularly polymerized to a very considerable extent would indicate in accordance with the views of Nernst[1] and Brühl[2] that the pure acid should have a large dielectric constant and high dissociative power. The specific inductive capacity of sulphuric acid has not been determined and no measurements of the electric conductivity of salts dissolved in it have been made. The electric conductivity of a concentrated acid may, indeed, be regarded as due to the ions of water, for the acid may be considered to be the solvent and water the dissolved substance. If the dielectric constant of pure sulphuric acid should be found to be larger than that of water, it seems in the light of the views of Nernst and Brühl quite natural to suppose that the acid would exert a not inconsiderable dissociative power on water. Still even in concentrated acid, the extraordinary dissociative power of water would assert itself, and the acid regarded as solvent would become dissociated into its ions in part. The circumstance that the acid may dissociate into more than two ions together with the probability that it is molecularly polymerized, complicates matters greatly.

The fact found by Kohlrausch[3] that a 10 per cent. solution of water in sulphuric acid presents a maximum of conductivity may perhaps be taken as an indication that the acid actually does assert a dissociative action on water ; that the conductivity of stronger solutions of acid in water are quite small may be due to the great viscosity of the acid solvent. It would be premature, however, to enter more at length into discussions of this nature, because of the fewness of the data and because the work of Kahlenberg and Lincoln[4] shows that not so very much reliance can be placed on the views of Nernst and Brühl.

[1] *Ztschr. phys. Chem.*, 13, 3 (1894).
[2] *Ibid.*, 18, 514 (1895) and 27, 317 (1898).
[3] Pogg. *Ann.*, 159, 233 (1876).
[4] *J. Phys. Chem.*, 3, 12 and 457 (1899).

ON HUBL'S IODINE METHOD FOR OIL ANALYSIS.

BY AUGUSTUS H. GILL AND WALTER O. ADAMS.

THIS method, as is well known, depends upon the fact that the unsaturated glycerides in the oils form addition products with iodine: it has the disadvantage that substitution products—the amount varying with the time of action and strength of the solution—are formed as well. If their formation could be prevented the test would be much increased in value and it was to ascertain if this were possible that this investigation was undertaken.

As ordinarily prepared, the solution contains mercuric chloride and iodine in alcohol: by their interaction mercuric chloriodide and iodine chloride are formed[1] and it is supposed that the latter is the active agent.

$HgCl_2 + I_2 = HgClI + ICl$. Ephraim[1] and also Wijs[2] have shown that practically the usual iodine numbers are obtained when a solution of iodine chloride in alcohol is employed. Schweitzer and Lungwitz[3] found that mercuric bromide caused a larger iodine number than the chloride: "that manganese bromide, cadmium, nickel and cobalt chlorides cause practically no addition[4] and that the latter gives the highest true iodine addition figure." As with mercuric chloride, there is no reason why mercuric bromide might not similarly form iodine bromide and this be the active agent.

These metallic salts may play another part in the reaction besides the formation of iodine chloride, that of carriers of halogen, similiar to that played by mercury in the Kjeldahl process when dissolving the substance in sulphuric acid. That some such agent is necessary, is shown by the results of Gantter,[5] who found that a solution of iodine in carbon tetrachloride acts very slowly upon the oil and that the results are irregular,— a result which the authors can substantiate, both with oils and oleic acid.

The substance selected as a carrier in the following experiments

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1 *Ztschr. angew. Chem.*, 284 (1895).
2 *Ber. d. chem. Ges.*, 31, 750.
3 *J. Soc. Chem. Ind.*, 14, 1031.
4 It would seem as if this should be "substitution."—Author.
5 *Ztschr. anal. Chem.*, 32, 181.

was mercuric iodide, and as it is more soluble in methyl than ethyl alcohol the former was employed : that used was free from acetone and anhydrous, being distilled from quicklime.   Thirty grams of mercuric iodide and 25 grams of sublimed iodine were dissolved in a liter of methyl alcohol; of this solution 30 cc. were employed for each test and the customary procedure followed. Oleic acid and various oils were used to test the efficacy of this solution ; the oleic acid was the purest obtainable, and gave no test for stearic acid.

The results are given in the accompanying table :

AMOUNT OF IODINE ABSORBED BY VARIOUS ACIDS AND OILS.

A. Acids.

Substance.	Time. Hrs.	Hübl.		Iodide.
Stearic Acid.	4	8.99		7.25
		8.70		6.97
		8.82		6.93
Average.		8.84		7.05
Oleic Acid.	4	101.0	91.31	89.19
		100.9	89.64	89.39
		103.5	90.93	90.54
Average.		101.7	90.2	
	3	—.	89.10	89.23
	20	99.38[1]		97.88[1]
		98.41		97.50
		98.37		97.65
	25	——		98.02
				97.70
				97.88

B. Oils.

Substance.	Time. Hrs.	Hübl.	Iodide.		
Olive.	4	82	78.9	79.0	79.3
Cottonseed.	4	107	91.6	91.2	92.9
Prime lard.	4	74	72.4	71.6	71.5
Neatsfoot.	4	59	55.8	56.0	55.6

It will be noticed in the case of stearic acid, which should have no iodine absorption, that the substitution, while not

[1] As is evident, considerable substitution has taken place here : this when corrected for gave the theoretical value, 90. This is at variance with the observation of Schweitzer and Lungwitz, *loc. cit.*, 1034.

entirely avoided, is materially lessened by about 20 per cent. With oleic acid, the numbers obtained by the iodide process average but 0.2 per cent. higher than the theoretical, 90 per cent., which is the closest agreement, so far as known, obtained by any process; they are 11 points lower than those obtained by the usual Hübl process. A slight substitution did occur as shown by the hydriodic acid liberated. This was increased by lengthening the time of action of the solution, as seen from the 20- and 25-hour tests; the 3-hour test was conducted to determine if the substitution could not be eliminated by a shorter time. It was found that it did take place, indicating apparently that substitution and addition occur simultaneously : a small amount of substitution was found in the case of the oils as well as with oleic acid.

Attention was called in the early part of this paper to the fact that alcoholic solutions of iodine caused a low and variable addition of halogen to oleic acid ; this is more particularly the case if carbon tetrachloride be used as a solvent; chloroform seems to increase this addition very materially. With the former, 66.74, 67.32, and 65.46 per cent. of iodine were added to oleic acid, whereas with the latter, 89.02, 83.66, and 85.86 per cent. were added.

As the solution used contained no halogen but iodine, thus excluding the formation of halides of iodine, and no water, excluding the liberation of oxygen, it would seem that we had here a method which, while as ready of application as the original Hübl, possessed the additional advantage of giving the true iodine figure.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
     BOSTON, November, 1899.

THE IODOMETRIC DETERMINATION OF SMALL QUANTITIES OF CARBON MONOXIDE.

BY LEONARD P. KINNICUT AND GEORGE R. SANFORD.

IN a previous paper[1] one of us mentioned that there might be more danger to be apprehended from the continuous breathing of air containing very small amounts of water gas, such as

1 Municipal Engineer, 17, 71.

might occur from imperfection in gas fittings than from sewer gas or arsenical wall papers. It is known that air containing 0.3 per cent. of carbon monoxide causes death, 0.2 per cent. very dangerous symptoms, and that mice quickly show the effect of the gas when the air contains only 0.05 per cent. There is reason to believe that air containing even much smaller quantities when breathed for a number of hours may have an effect on the human organism, and on this account the detection and quantitative determination of very small amounts of carbon monoxide when mixed with large volumes of air is a question of importance.

The methods of detecting and estimating very small amounts of carbon monoxide may be divided into two classes : first, those in which carbon monoxyhemoglobin is formed ; second, those in which it is oxidized to carbon dioxide. Those of the first class are of little value except for the detection of the gas and they may all be considered as modifications of Hoppe-Seyler's method, first published in 1864,[1] which is based on the fact that while both carbon monoxyhemoglobin, formed by the action of carbon monoxide on arterial blood, and oxyhemoglobin, give two absorption bands in the spectrum ; oxyhemoglobin is alone reduced to hemoglobin by the action of such reducing agents as ferrous sulphate or ammonium sulphide.

The method of determining carbon monoxide by oxidation to carbon dioxide has not, until the past few years, received much attention. This oxidation can be accomplished by the use of many oxidizing agents, but of all of those which have been proposed iodine pentoxide is, from our experience, the one that can best be used for the determination of small amounts of carbon monoxide.

Ditte,[2] in 1870, showed that at temperatures between 150°–200° iodine pentoxide was decomposed by carbon monoxide, iodine and carbon dioxide being formed.

$$I_2O_5 + 5CO = I_2 + 5CO_2.$$
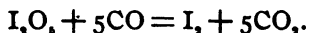
This reaction was seemingly first used by C. de la Harpe and F. Reverdine[3] for the detection of the gas, and Nicloux[4] and

[1] Ztschr. anal. Chem., 3, 439 (1864).
[2] Bull. Soc. Chim., 13, 318 (1870).
[3] Chem. Ztg., 12, 1726 (1888).
[4] Compt. rend., 126, 746.

Gautier[1] have made use of the reaction for its quantitative determination.

Nicloux determined the iodine set free, by the depth of color formed in a chloroform solution, and Gautier by the amount of carbon dioxide formed. We have not, by either of these methods, been able to obtain accurate determinations of small amounts of carbon monoxide, but have obtained most satisfactory results by determining the amount of iodine set free, with an N/1000 solution of sodium thiosulphate.

The apparatus used was, with slight changes, that described by Nicloux. Twenty-five grams of iodine pentoxide were placed in a small U-tube, which was suspended in an oil-bath and connected with a Wolff blood absorption tube containing 0.5 gram potassium iodide dissolved in 5 cc. water. The tube containing the iodine pentoxide was also connected with two U-tubes, one containing sulphuric acid, the other small pieces of potassium hydroxide, so as to remove from the air to be analyzed before it came in contact with the iodine pentoxide all unsaturated hydrocarbons, hydrogen sulphide, sulphur dioxide, and similar reducing gases. In all the experiments the oil-bath in which the U-tube containing the iodine pentoxide was suspended, was heated to 150° C., as preliminary tests showed that the reaction was not a quantitative one at lower temperatures.

The iodine pentoxide was made by the action of nitric acid on resublimed iodine, and after this substance had been purified by the usual methods the last traces of free iodine were removed by passing air, freed from all reducing substances, through the iodine pentoxide contained in a U-tube heated to 150° C.

In the experiments which were made to determine the accuracy of the above process, 1 liter of air was usually taken, but as seen in the following tables amounts as small as 250 cc. were tried in several cases and the rate at which the air was passed through the tubes was about 1 liter in two hours, the rate being controlled by forcing the air out of the bottle in which it was contained by dry redistilled mercury, the flow of which was regulated by a glass stop-cock. The amount of carbon monoxide added to the air was accurately measured from a tube made of capillary glass tubing and accurately calibrated so that each

[1] *Compt. rend.*, 126, 931.

division represented 0.005 cc., and readings of 0.001 cc. could easily be made. The temperature and barometric pressure were carefully noted and all volumes were reduced to 0° C. and 760 mm. pressure, and the determination of the iodine set free was made in the Wolff blood absorption apparatus which contained the potassium iodide solution.

With this apparatus, used as described, we were able to determine as small an amount as 0.025 cc. of carbon monoxide, when contained in 1000 cc. of air, or 0.0025 per cent. by volume. The following table gives the results obtained:

ANALYTICAL RESULTS.

Volumes taken.		Iodine liberated.		
Air.	Carbon. monoxide.	Theoretical.	Found.	Difference.
cc.	cc.	Mg.	Mg.	Mg.
1000	0.410	0.941	0.907	0.034
1000	0.286	0.6575	0.6375	0.020
1000	0.359	0.8178	0.7832	0.0346
1000	0.170	0.3859	0.4540	0.0081
1000	0.211	0.4809	0.4775	0.0034
1000	0.151	0.3442	0.3252	0.019
1000	0.115	0.2639	0.2758	0.012
1000	0.061	0.1391	0.1431	0.004
1000	0.023	0.0535	0.0494	0.0041
1000	0.029	0.0672	0.0689	0.0017
1000	0.023	0.0535	0.0495	0.004
500	0.131	0.2993	0.2976	0.0017
250	0.030	0.06862	0.07165	0.0029
250	0.026	0.05967	0.05855	0.0011

Volumes taken.		Carbon monoxide.		
Air.	Carbon monoxide	Calculated. Per cent.	Found. Per cent.	
cc.	cc.	By volume.	By volume.	Difference.
1000	0.410	0.041	0.0395	0.0015 —
1000	0.286	0.0286	0.0278	0.0008 —
1000	0.359	0.0359	0.0341	0.0018 —
1000	0.170	0.0170	0.0197	0.0027 +
1000	0.211	0.0211	0.0208	0.0003 —
1000	0.151	0.0151	0.0142	0.0009 —
1000	0.115	0.0115	0.0119	0.0004 +
1000	0.061	0.0061	0.0062	0.0001 +
1000	0.023	0.0023	0.0021	0.0002 —
1000	0.029	0.0029	0.0030	0.0001 +
1000	0.023	0.0023	0.0022	0.0001 —
500	0.131	0.0262	0.0260	0.0002 —
250	0.030	0.0120	0.0124	0.0004 +
250	0.026	0.0104	0.0100	0.0004 —

These results showed that by the above method accurate determinations could be made of very small amounts of carbon monoxide in pure air, and it only remained to be proved that the accuracy of the process was not affected when the carbon monoxide was mixed with air containing illuminating gas, and experiments were made to determine the action of hydrogen, marsh-gas, unsaturated hydrocarbons, hydrogen sulphide, and sulphur dioxide on iodine pentoxide.

Hydrogen and marsh-gas, as was to be expected, had no effect on the iodine oxide at 150°C. and the unsaturated hydrocarbons, hydrogen sulphide and sulphur dioxide, in much larger amounts than are contained in illuminating gas, or formed by its combustion, were perfectly absorbed, when passed in the way described through ∐-tubes containing sulphuric acid and potassium hydroxide.

These facts having been determined, mixtures of illuminating gas and air were made, and the amount of carbon monoxide determined.

The experiments gave the following results :

The gas used contained 18.6 and 19.0 per cent. of carbon monoxide, respectively. Of the first, 0.104 cc. was added to 1 liter of air and the air was found to contain 0.019 cc. carbon monoxide, the calculated amount being 0.0191 cc. In the second case, 0.146 cc. of the gas was taken and the air gas found to contain 0.027 cc. of carbon monoxide in place of 0.02789 cc.

The results that have thus been obtained show that the presence and amount of carbon monoxide in the air of a room can be determined when the air contains above 0.0025 per cent. by volume, or 2.5 volumes in 100,000 volumes of air, and if the presence of this gas is due to leakage of illuminating gas and the per cent. of carbon monoxide in this gas is known, the amount of illuminating gas contained in the air can, of course, approximately be calculated.

THE TECHNICAL ANALYSIS OF LICORICE PASTES.

BY M. TRUBEK.

WHEN I was first confronted with the analysis of licorice products, I had to select a method, which, giving the necessary data required by the trade, could easily be carried out in a reasonably short time.

The literature on that subject was found to be rather meager and only fragments could be found here and there. More comprehensive was the article on the subject of licorice found in Hager's *Pharmaceutische Praxis*, and for the determination of some constituents the method therein described was at first carried out with a few minor modifications; instead of taking 10 grams of substance as prescribed only 2 grams were used. The first amount required too large quantities of ammonia and alcohol on one hand and absolute alcohol on the other hand to get a colorless filtrate, besides requiring too much time, extra large filters and weighing-bottles. It soon developed, however, that the above method gave too high results in glycyrrhizin, which results were out of question, in case glucose had been added to the paste, as the following figures will show :

	Glycyrrhizin. Per cent.
1. Paste with no glucose added	22.25
2. Same paste with 15 per cent. glucose added	29.61
3. " " " 20 " " " "	34.12

Instead of going down on glycyrrhizin as it should be through the addition of the glucose, the values for that substance rose with the amount of glucose added. It was examined for that substance as glucose might have been thrown down together with the glycyrrhizin and was not entirely removed during washing, by precipitating the glycyrrhizin with basic lead acetate but only about 2 per cent. of glucose were found in No. 2, not explaining the rise in glycyrrhizin. I concluded therefore that that rise was due to the presence of a substance or substances formed from the glucose by the ammonia, especially while concentrating the run-off from the first operation, which substances were absolutely insoluble in absolute alcohol and could not be washed out by the same. After several experiments along those lines the following mode of operation was adopted and found to work satisfactorily.

To 2 grams of the extract to be examined add 5 cc. water, place on a warm plate, and by means of a glass rod make up to a perfectly even mass. Add little by little, while stirring, 20 cc. of 96 per cent. alcohol and allow to settle. Filter through a weighed filter and wash with a mixture of 1 part water and 4 parts alcohol of above strength until run-off is colorless, which takes about 100 cc. of wash liquor. Keep the top of the filter wet, as it easily dries out and is then washed with difficulty. The filter, with contents, is dried at 105° C. for three hours and weighed. It gives the gummy matter, starch, etc., contained in the extract. The filtrate is either distilled off or evaporated. Take a large beaker for evaporating, or ·else liquor creeps up to the edges incurring losses. When nearly evaporated transfer to a small beaker, evaporate further to a thick sirup, making about 1 or 1.5 cc. It is then dissolved in 2 cc. glacial acetic acid, and 30 cc. absolute alcohol are added with constant stirring. Too violent stirring produces a lumpy mass, which is difficult to wash out. The solution is allowed to settle. Filter through a weighed filter, wash with absolute alcohol until no acid reaction, dry at 105° C. for three hours, and weigh. The figure obtained is not pure glycyrrhicic acid, but rather a salt. To get the acid sufficiently accurate, an aliquot part is incinerated, using blast heat at the end, and deducting 0.7 of the percentage of ash from the percentage of the salt found. The ash consists mainly of calcium oxide, but contains also very small amounts of alumina and magnesia.

The glycyrrhizin salt as prepared by my method represents a light yellow amorphous powder, soluble in glacial acetic acid, cold and hot water, and dilute alcohol. It has a very sweet taste. (The pure glycyrrhicic acid is according to Haberman[1] a tribasic acid and forms acid and normal salts. It dissolves in the same reagents as the salt above described, but only in hot water, while making a jelly with cold water.)

The filtrate from the glycyrrhizin is distilled off, diluted and evaporated, and this repeated until the acetic acid is driven off. The residue is dried at 105° C. for three hours and weighed. This amount represents the so-called extractive matters, containing the saccharine matter that the root contained originally or which had been added subsequently to the paste; they contain also some tannin, resin, etc.

[1] *Ann. Chem.* (Liebig), 197, 105.

Ash, in the paste, is determined by incinerating 2 grams in a platinum dish.   For total solids, about 5 grams are dissolved in hot water and made up to 500 cc. after cooling the liquor.   It is well shaken and 50 cc. are evaporated, dried at 105° C. for three hours, and weighed.

For solids soluble in cold water, 50 cc. of the clear filtrate are evaporated, dried, and weighed. For evaporation, flat bottomed, so-called crystallizing glasses have been found to be very convenient.

The difference between " total solids" and "soluble solids" represents the residue insoluble in cold water.

The moisture is taken as the amount obtained by subtracting the "total solids" from 100.

Reducing substances are determined as usual after precipitating with basic lead acetate and titrating the filtrate, freed from lead, with standardized Fehling's solution.

Following are the results obtained by the above method from different samples of licorice extract :

	1. Per cent.	2. Per cent.	3. Per cent.	4. Per cent.
Moisture	24.18	25.14	19.58	23.99
Residue insoluble in cold water·	3.95	6.79	14.35	2.54
" " " mixture of				
1 water and 4 alcohol	27.27	25.20	36.58	24.65
Glycyrrhizin	22.78	21.97	18.51	19.90
Extractive matter	25.02	25.05	26.02	28.91
Ash	6.25	6.02	5.60	5.59
Reducing matters as glucose	....	....	....	9.76

Sample No. 1 was one of Scudder's brands.

Sample No. 4 gave, by the method described in Hager's *Pharmaceutische Praxis* for glycyrrhizin, 28.57 per cent.

An analysis of fresh and spent licorice root gave the following results :

	Fresh. Per cent.	Spent. Per cent.
Moisture	8.40	10.00
Total solids	33.18	10.86
Cold solubles	29.65	....
Gummy matter, starch, etc	8.07	3.56
Glycyrrhizin	11.21	2.25
Extractive matters	14.77	5.60
Ash	2.68	0.55
Reducing matters	0.52	....

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BENZENESTEAROSULPHONIC ACID AND OTHER SUL-PHONIC ACIDS CONTAINING THE STEARIC RADICAL.[1]

BY E. TWITCHELL.

I N connection with some experiments on the action of sulphuric acid on the higher fatty acids I prepared a mixture of benzene and oleic acid and treated this with an excess of concentrated sulphuric acid. I found that a union took place between the benzene and the oleic acid, and at the same time a sulphonic acid was formed.

$$C_6H_6 + C_{18}H_{34}O_2 + H_2SO_4 = C_6H_4(SO_3H)C_{18}H_{34}O_2 + H_2O.$$

To prepare this benzenestearosulphonic acid, a mixture of oleic acid and benzene is treated with a large excess of concentrated sulphuric acid, avoiding any excessive rise in temperature by cooling the mixture and by adding the acid slowly. After several hours the greater part of the oleic acid will have combined as expressed by the above equation, and the benzene-stearosulphonic acid can be separated and freed from the excess of the original components of the mixture and from the results of secondary reactions which have occurred.

A consideration of the action of sulphuric acid on oleic acid will make it plain that these impurities can only be the following :

1. Unacted-on oleic acid;

2. Other fatty matters, such as oxystearic acid and fatty anhydrides, produced by the action of the sulphuric acid and subsequent decomposition of the sulpho compounds;

3. Unacted-on benzene ;

4. Stearosulphuric acid, $C_{18}H_{35}O_2.HSO_4$;

5. Benzenesulphonic acid;

6. Sulphuric acid in large excess.

From its mixture with these substances the pure benzene-stearosulphonic acid can be separated by virtue of the following properties it possesses, to which I will again refer: It is soluble

in water, but can be rendered completely insoluble (salted out) by the presence in the water of a little hydrochloric acid or sulphuric acid. It is very stable, not decomposed by boiling with acid solutions. It is insoluble in petroleum ether.

The reaction mixture is treated with water and heated to boiling, whereby the excess of sulphuric acid is diluted and the mass separates into two layers; the lower, a clear aqueous liquid, contains the excess of sulphuric acid and whatever benzenesulphonic acid may have been produced. The upper layer, a viscous oil, contains the benzenestearosulphonic acid with the remaining impurities insoluble in dilute sulphuric acid. If any stearosulphuric acid was present, this will have been decomposed by the heating into sulphuric acid and oxystearic acid and anhydrides. The lower layer is removed and the upper is washed with water containing hydrochloric acid until free from sulphuric acid. By this operation the benzene-sulphonic acid is also washed out. The oily layer is now washed a number of times with petroleum ether, which dissolves the oleic acid, the benzene, and the other fatty matters before mentioned, leaving the compound pure except for small quantities of water and hydrochloric acid, and these can easily be removed by drying at 100° C.

The washing with petroleum ether is a tedious process, as some of the decomposition products of oleic acid are rather difficultly soluble in this liquid. For this reason, when quantitative results are not required, it is better to dissolve the partially purified product in ether and shake with water. The aqueous extract, containing most of the benzenestearosulphonic acid, is treated with a little hydrochloric acid, taken up with ether and again extracted with water. On evaporating the aqueous solution the compound is obtained in a pure state.

The composition of the compound was determined by the estimation of the sulphur and carbon and by its acid equivalent, it being a dibasic acid containing an acid hydrogen of the sulphonic radical, which can be exactly titrated by using methyl orange as indicator, and an acid hydrogen of the fatty radical which can be titrated with phenolphthalein as indicator.

The several analyses represent samples prepared at different times.

	Sulphur.	Carbon.	Ratio of sulphur to carbon.	$n/10$ alkali required to combine with SO_3 H group in 1 gram of substance. Methyl orange as indicator. cc.	Additional $n/10$ alkali required to combine with the fatty group. Phenolphthalein as indicator. cc.
Calculated for					
$C_{10}H_6.SO_3H.C_{18}H_{35}O_2$.	7.2727	65.45	9.00	22.727	22.727
Found 1				21.56	22.41
" 2	7.12			22.49	22.44
" 3	7.22	64.70	8.96	22.66	23.19

The composition was further fixed by the determination of the weight of benzenestearosulphonic acid obtained from the oleic acid which entered into the reaction. From the molecular weights of the two compounds, 282 parts of oleic acid would yield 440 parts of benzenestearosulphonic acid, or the yield on 100 parts of oleic acid would be 156.03.

An accurately weighed, quantity of oleic acid was mixed with benzene and then treated with an excess of sulphuric acid. After removing the impurities soluble in acidified water, the product was extracted with petroleum ether, the extract weighed and deducted from the amount of oleic acid taken. The difference was that which had combined with benzene and sulphuric acid. The residue insoluble in petroleum ether was also dried and weighed, giving the yield of benzenestearosulphonic acid.

In two experiments 100 parts of oleic acid were found to yield 151.0 and 156.7 parts of benzenestearosulphonic acid.

In this calculation there is an error, in that the petroleum extract does not consist wholly of unaltered oleic acid, but also contains oxystearic acid and anhydrides; but this error is very small considering the small quantity of oleic acid deducted as a correction, and the fact, established by an experiment, that the weight of the fatty matter is only slightly altered on treating oleic acid alone with sulphuric acid and then decomposing by boiling with water.

Benzenestearosulphonic acid resembles in its physical characteristics, and also in many of its chemical ones, the stearosulphuric acid obtained by acting on oleic acid in the cold with concentrated sulphuric acid. At 100° C. the dry compound is a very viscous oil, while at ordinary temperatures it is a sticky, semisolid mass. It, as well as its mono- and di-alkaline salts,

is soluble in water in all proportions, yielding colloidal solutions which, on agitating, form a strong lather and are precipitated (salted out) by any strong acid, base or salt. The free acid is perfectly stable in boiling water, even in the presence of mineral acids, differing in this from stearosulphuric acid. On heating to high temperatures with hydrochloric acid it decomposes only very slowly. A small quantity heated in a sealed tube to 170° C. for three and a half hours, had decomposed only to the extent of 15 per cent.

Benzenestearosulphonic acid when fused with caustic potash gives potassium sulphite. Here again it differs from stearosulphuric acid, which when similarly treated yields potassium sulphate.

As shown by the formula, benzenestearosulphonic acid is dibasic, the two acid hydrogens having very different strengths, so that, as has been already pointed out, they can be independently titrated with caustic soda solution, using different indicators.

NAPHTHALENESTEAROSULPHONIC ACID,

$$C_{10}H_6 (SO_3H) C_{18}H_{35}O_2.$$

This compound is prepared and purified in a manner precisely similar to that used in the preparation of the benzene compound, which it closely resembles, being, however, rather less fluid in its character.

The analysis gives the following results:

	$n/10$ alkali required to combine with the SO_3H group in one gram of substance. Methyl orange as indicator. cc.	Additional $n/10$ alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator. cc.
Calculated for $C_{10}H_6.SO_3H.C_{18}H_{35}O_2$	20.408	20.408
Found 1	20.07	19.97
" 2	20.28	20.17
" 3	20.35	20.41

PHENOLSTEAROSULPHONIC ACID,

$$C_6H_4OH (SO_3H) C_{18}H_{35}O_2.$$

This compound is prepared like the others and closely

resembles them in its character. The following analytical results show that the compound had not been obtained pure.

	n/10 alkali required to combine with the SO$_3$H group in 1 gram of substance. Methyl orange as indicator.	Additional n/10 alkali required to combine with the fatty group in 1 gram of substance. Phenolphthalein as indicator.
	cc.	cc.
Calculated for C$_6$H$_3$OH.SO$_3$H.C$_{16}$H$_{35}$O$_2$.	21.929	21.929
Found 1	24.47	20.39
" 2	29.75	20.77

These results clearly indicate the presence of ·a disulphonic acid. This I have not yet attempted to separate, but its quantity can be calculated and allowed for, and if this is done it will be seen that the figures will agree closely with those required by the formula.

In much of the analytical work described in this paper and also in the preparation of some of the compounds, I was kindly assisted by Mr. Wm. Simonson.

A NEW INTERRUPTER FOR THE KOHLRAUSCH-OSTWALD CONDUCTIVITY METHOD.

BY J. LIVINGSTON R. MORGAN. .

IN a recent paper[1] I described three useful additions to the Kohlrausch-Ostwald conductivity method. Since then an improvement has been made in the interrupter, the first of the three described, which simplifies it to such an extent that a description of it is deemed advisable. In the apparatus as first proposed, the primary current (2–5 volts from the electric light circuit or from storage cells) was used to charge the vibrating wire as well as to excite the electromagnet. The current from the cell used in the conductivity apparatus was then connected, through the vibrating wire and an extra mercury cup, to a small induction coil (without the breaker), the secondary of the coil being connected to the bridge arrangement in the usual way. The intermittent current produced by the vibrating wire and the mercury cup becomes a rapidly alternating one, such as is desired, in passing through the induction coil.

[1] This Journal, 22, 1 (1900).

In the new form, one of the mercury cups is dispensed with entirely, and the current from the cell of the conductivity apparatus alone goes through the wire causing it to vibrate, and thus with the mercury cup to make and break the circuit. In the Pupin arrangement[1] using the permanent magnet, one cell is
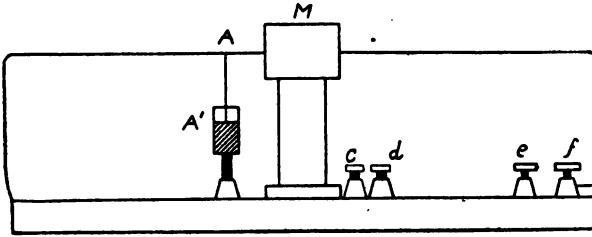
Fig. 1.—*c* and *d*, the binding posts of the electromagnet, are connected to the electric light circuit (3 to 5 volts). *c* is connected under the base to the mercury cup *A'*.

insufficient to cause a vibration but by the use of an electromagnet the strength of the magnetic field can be so intensified that the wire is repelled even when carrying a very small current. Fig. 1 shows the arrangement of the new form of
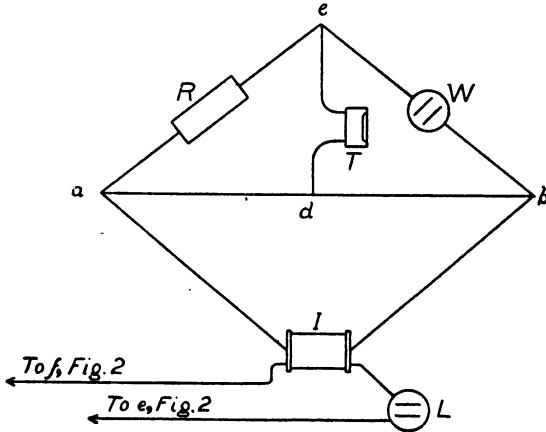
Fig. 2.—R is the known resistance, W the electrolytic cell, I the coil, L the Lelanché cell and T the telephone. The current breaker of the coil I is removed.

apparatus. The electromagnet is excited by a current of from 2 to 5 volts entering at the posts *c* and *d*. The current from the battery *L* (Fig. 2) is connected to the primary of the induction coil *I* through the posts *e* and *f* (Fig. 1). The dipper of the

wire *A* is in contact with mercury *A'* in the adjustable cup, which is connected by a wire under the base to the post *e*.   The current then goes from one pole of the battery *L* to *f*, *A*, *A'*, *e* and then through the primary of the induction coil back to the other pole. When the current is passing through the wire the magnet will repel the wire, and if the cup *A'* is at the proper height the contact with the mercury will be broken and since the wire when uncharged is not affected by the magnet its tension will make the contact once again and the same process will be repeated.   The tension of the wire and consequently the rapidity of vibration, may be altered by the screw devices at each end.

This new form of apparatus is not only simpler in construction than the original, but is also much more readily adjusted and kept in adjustment.   In the earlier form with two mercury cups it is necessary that the wire vibrate in such a way that loops are formed at the two cups, so that the original adjustment is more difficult to make and a variation in the number of vibrations per second is less easy to arrange.   If three or more pieces of conductivity apparatus, each with its cell, are connected to the same vibrator, a smaller voltage may be used for the electromagnet, for the voltage in the wire is much greater and consequently the strength of the magnetic field may be much reduced and still give the same result.

THE SPECIFIC GRAVITY AND ELECTRICAL RESISTANCE OF METALLIC TELLURIUM.

BY VICTOR LENHER AND J. LIVINGSTON R. MORGAN.

IN this Journal[1] one of us described the preparation of metallic tellurium by means of the reduction of an alkaline solution of the oxide of tellurium with sugar. A description was given in that paper of the means used to test the tellurium for impurities.   The tellurium obtained by reducing with sugar was found to be volatile in hydrogen gas leaving no residue.   Its oxide was found to be completely volatile in hydrochloric acid gas.

[1] Lenher: This Journal, 21, 348.

As a further means of establishing the purity of the metal, a few physical tests were made. The specific gravity was carefully determined and a great deal of time was spent in attempting to determine its electrical resistance.

Determination of the Specific Gravity.—For this purpose, material was selected, which had been twice distilled in hydrogen.

The metal was finely powdered, as a number of preliminary experiments showed that owing to the great crystalline tendency that the metal exhibits, it is almost impossible to obtain a specimen of any size which does not contain gas. Consequently, it was found that reasonably constant results could be obtained only when the metal was carefully broken up.

The experiments were carried out in an ordinary 15 cc. pycnometer, pure water being used as the medium. The temperature was 20°. In order to expel the adhering air bubbles, the water with the metal was heated and the vessel allowed to stand over night to cool.

	Weight tellurium taken.	Sp. gr.
Experiment 1....	11.9727	6.194
" 2	11.9146	6.200
" 3	16.0946	6.204
Mean		6.1993

This figure is a trifle less than that obtained by Spring[1] but is almost identical with that obtained by Klein and Morel[2]. The latter chemists obtained the figures 6.204 and 6.215, while Spring obtained a figure slightly higher, 6.22.

The latest figure previous to our work is by Priwoznik[3] who obtained 6.2459 at 18.2°.

Determination of the Electrical Resistance.—For the determination of the electrical resistance of a metal, it is advisable to obtain great length and small diameter of the substance. With tellurium this is almost impossible. The metal is extremely crystalline, more strongly so than any metal which has come into our hands. As a result of this tendency, the metal, when of small diameter and possessing any appreciable length, is so weak that a rod grasped by the end will snap off, it not being able to sustain its own weight.

[1] *Bull. Acad. Roy. Belg.* [3], **2**, 88-110 (1881).
[2] *Ann. Chem.* (Liebig), [6], **5**, 61.
[3] *Chem. Centrbl.*, **2**, 962 (1892).

It is not practical to cast the metal in cold moulds. Various attempts were tried in this direction but proved unsuccessful. The best method for obtaining a suitable section was found to be to melt the metal in a thin glass tube of comparatively narrow bore. To this end an open glass tube was placed in an inclined combustion furnace and inside of it was introduced a smaller tube closed at one end and containing the metal to be fused. The fusion took place at a low red heat, while in the liquid condition, the tube was gently tapped until all of the gas escaped.

Slow cooling tends to produce larger crystals and the metal is correspondingly more brittle. Rapid cooling, on the other hand, gives smaller crystals, but the difference in resistance is not apparent. The most satisfactory results were obtained by jacketing the tube of molten tellurium with a larger tube also containing fused metal. Although in this instance the metal cooled under the pressure of the shell in the jacket, the only apparent difference was that longer sticks could be obtained.

From the many fusions that have been made in this laboratory, it appears that tellurium on cooling, first contracts until it solidifies, then slightly expands. As an example of this may be noted that each stick contained a depression in its upper part, which extended about one-fifth of the entire length[1] and that the tubes always cracked just after the metal solidified. The tubes invariably cracked at this time, no matter how carefully they had been annealed, nor how slowly they were cooled.

In order to obtain the best possible contact, a piece of rubber tubing was drawn over each end of the stick to be measured and the tubes filled with mercury. The latter was connected with a small dry battery, a wheatstone bridge and galvanometer being in the circuit.

No. 1.—Length, 100 mm., diameter, 7.42 mm. Resistance at $20° = 1.38$ legal ohms. Specific resistance = 596.6.

No. 2.—Length 162 mm., diameter, 8.89 mm. Resistance at $20° = 1.23$ legal ohms. Specific resistance = 463.6.

No. 3.—Length, 137 mm., diameter, 8.255 mm. Resistance at $20° = 1.46$ legal ohms. Specific resistance = 569.9.

No. 4.—Length, 103 mm., diameter, 3.43 mm. Resistance at $20° = 3.68$ legal ohms. Specific resistance = 330.1.

[1] This portion was always removed before measurements were made.

No. 5.—Length, 82 mm., diameter, 3.43 mm. Resistance at 20° = 2.48 legal ohms. Specific resistance = 279.4.

This specimen was a piece of No. 4 after a portion had been broken off.

No. 6.—Length, 84.5 mm., diameter, 3.05 mm. Resistance at 20° = 5.88 legal ohms. Specific resistance = 508.3.

No. 7.—Length, 86.1 mm., diameter, 4.83 mm. Resistance at 20° = 5.37 legal ohms. Specific resistance = 1152.

On close examination this bar was found to be cracked.

No. 8.—Length, 57.5 mm., diameter, 2.92. Resistance at 20° = 4.68 legal ohms. Specific resistance = 544.5.

As all of the bars showed a strong cleavage on the ends, the measurements could only be approximate, and when they are calculated to the standard conditions, one meter in length, with a cross section of one mm., the errors of measurement are correspondingly multiplied.

By using an ordinary copper clamp contact, almost any resistance can be obtained according to the amount of pressure exerted by the clamp ; no difference in resistance could be detected when working in the light or dark.

By comparison of the results obtained, it will be observed that the mean would be about 500 ; however, from the great tendency to crystallization that the metal shows, it would seem more probable that the lowest result more nearly approaches the true figure. As gas carbon has a specific resistance equal to 50, the resistance of tellurium is seen to be enormous. The result obtained by Matthieson,[1] 0.000777 for the conductivity compared with silver as 100, would give a specific resistance of more than 2000, showing that the structure of his metal must have been different from ours or that different contact was made.

THE VOLUMETRIC DETERMINATION OF MAGNESIA.

By JAMES OTIS HANDY.

Received January 2, 1900.

EVERY chemist, who has to make many determinations of magnesia in water, cement or other material, appreciates the difficulties surrounding the gravimetric process. These difficulties chiefly arise from the fact that the change from magne-

[1] *Pogg. Ann.*, 103, 428.

sium ammonium phosphate to the pyrophosphate of magnesia is attended by a rapid consolidation or sintering of the mass. By this means particles of carbon from the filter-paper are often firmly enclosed in the lumps of precipitate.

If gradual heating over a Bunsen burner is continued long enough, fifteen minutes over the blast-lamp with crucible inclined and cover placed in a position to facilitate oxidation, will give a pure white pyrophosphate. If, however, the preliminary heating proceeds too rapidly, or is not continued long enough before applying the blast, it is almost impossible to burn off all the carbon.

The method recommended by Fresenius for completing the oxidation of such material by treatment with nitric acid followed by evaporation and re-ignition, yields a pure white residue, but the result is invariably low. The author found that pure magnesium pyrophosphate when so treated lost weight every time, although no mechanical loss took place. Moreover, repetition of the treatment caused further serious loss. Constant weight was not reached.

No one who has adopted the volumetric method for determining calcium oxalate by means of standard permanganate would ever go back to the gravimetric way. When a simple and accurate method for the volumetric determination of magnesia appears, it will be equally useful.

The alkalimetric method published by Stolba in 1866[1], referred to by Sutton, Hart, Meade[2] and others, has not come into general use. The reaction is:

$$MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4.$$
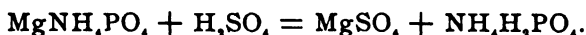
Its unpopularity is doubtless due to the use of alcohol for removing the ammonia wash from the magnesium ammonium phosphate precipitate, it being an expensive and tedious procedure.

Meade proposes a radical change from the usual phosphate method. He estimates the magnesia by precipitating it as arsenate and determines by standard thiosulphate the amount of iodine which a hydrochloric acid solution of the precipitated arsenate liberates from potassium iodide. The procedure seems

1 *Chem. Centrbl.*, 728 (1866).
2 This Journal, 21, 746 (1899).

rapid and accurate, but it would appeal only to those who prefer an iodometric to an alkalimetric method.

The writer has endeavored to eliminate the objectionable feature of Stolba's method by discarding alcohol and removing the free ammonia from the phosphate precipitate by taking advantage of the volatility of ammonia.

It was necessary to find some way of expelling the ammonia without in any way affecting the integrity of the phosphate which should remain. In view of the fact that Fresenius, Roscoe and Schorlemmer, and other authorities all agree that the only change which $MgNH_4PO_4.6H_2O$ suffers at 100° C., is the loss of 5 molecules of water of crystallization, it seemed a simple thing to put filter and precipitate into 50 cc. of distilled water, and after removing the ammonia by boiling down to 30 cc., to cool, add a measured excess of standard acid to dissolve the precipitate, and then to titrate back with standard alkali. After many trials in which the results were all low and irregular this method was abandoned. Evidently some change of composition took place at 100° C. under these conditions.   •

Other means of subjecting the ammoniacal precipitate to this temperature were tried. The filters containing the precipitates were spread out flat on strong 5-inch filters, and were placed, one set at a time, in a funnel through which a current of steam was rising, and allowed to remain for ten minutes. The ammonia was expelled, but the results by titration were still low, although absolutely no mechanical loss or loss by solution took place. There was a loss in alkalinity due to a chemical change other than the loss of water of crystallization.

Thinking that the presence of water in the one, and of steam in the other of these experiments, might have brought about a change which temperature alone could not have accomplished, a set of experiments were made wherein the filters and precipitates were dried in an oven at 100° C., away from all but the moisture which they at first contained. By this means also, low results were obtained.

It was then apparent that no rapid or satisfactory method could be based on titration of magnesium ammonium phosphate which had been dried at 100° C., or even heated to that temperature without drying. Although the change in alkalinity

might be perfectly definite and complete, it would require much longer for large precipitates to be completely transformed than for small ones, and irregular results would surely be obtained.

Before rejecting the statement of such eminent authorities with regard to the effect of drying magnesium ammonium phos-phate at 100° C., it was thought best to completely eliminate the moisture element from the experiment.

A quantity of the pure salt was prepared by precipitation under standard conditions from a solution of magnesium chloride. After washing thoroughly with 10 per cent. ammonia wash (1 part of ammonium hydroxide, sp. gr. 0.90, mixed with 9 parts of water), the precipitate was spread out on filter-paper and allowed to dry in the air. It was then dried over sulphuric acid, after which it was ground, mixed and placed in a stoppered bottle. Weighed portions were then tested for purity, and this having been established, the property in question was examined into.

PROPERTIES OF $MgNH_4PO_4.6H_2O$.

	Statement of authorities. Per cent.	Actual facts. Per cent.
Loss of weight at 100° C. (water, etc.)	36.70	41.43
Yield of $Mg_2P_2O_7$ on ignition.................	45.34	45.59
Cc. $\frac{N}{10}$ H_2SO_4 for 1 gram before 100° drying	82.05	81.94
The same if dried at 100° C. beforehand.......	82.05	54.59
Loss of original alkalinity at 100° C. (per cent.)	00.00	33.38

The author does not wish to be understood as saying that the first column in the above table represents verbatim the state-ments of Fresenius and others, but that it does represent the exact results which would follow if their statements were true.

By comparing the magnesium oxide value of decinormal sul-phuric acid when used on air-dried $MgNH_4PO_4.6H_2O$ with the value when a weighed amount of the same salt is heated to constant weight at 100° C. before titration, it will be seen that the difference is very great.

1 cc. $\frac{N}{10}$ H_2SO_4 = 0.002 gram MgO in the air-dried salt.

1 cc. $\frac{N}{10}$ H_2SO_4 = 0.003 gram MgO in the same material if first dried at 100° C.

Although the definiteness of this change is now firmly estab-lished, the formula of the compound which is formed at 100° C., has not yet been determined.

The folly of drying at 100° C. as a preliminary to the titration of $MgNH_4PO_4.6H_2O$ having been established, the author determined to ascertain the speed with which ammonia evaporated from phosphate precipitates at ordinary temperature. It was found that if filters containing precipitates were opened flat after washing, and placed face upward on heavy dry filter-paper of the sort made by Whitall, Tatum & Co., for druggist's use, the bulk of the moisture would be drawn out in a few minutes, and if transferred then to a second dry paper and allowed to stand for half an hour to one hour, the ammonia, so far as its power of neutralizing a measurable quantity of acid was concerned, had entirely disappeared. When the filter-papers have become dry for a distance equal to one-fifth of the diameter of the paper, measured from the outer rim, it is certain that the ammonia has been expelled. This is, of course, based on the assumption that the precipitate is distributed fairly evenly over the rest of the paper.

Methyl orange was the indicator used, and in all cases a clear yellow was considered the end-point when using decinormal sodium hydroxide to measure the excess of decinormal sulphuric acid.

TITRATION OF $MgNH_4PO_4.6H_2O$.

	Time for precipitation. Hrs. Min.		Time of drying. Hrs. Min.		Temperature.	MgO used. Gram.	MgO found. Gram.	Error. Gram.
1	3	0	18	6	21° C	0.00475	0.00478	0.00003
2	3	0	18	6		0.01900	0.01900	0.00000
3	3	0	18	6		0.02375	0.02377	0.00002
4	3	0	·18	6		0.04750	0.04785	0.00035
5	1	30	2	0	19	0.02375	0.02377	0.00002
6	1	30	2	30	19	0.02375	0.02377	0.00002
7	1	30	3	0	19	0.02375	0.02377	0.00002
8	1	30	3	20	19	0.02375	0.02377	0.00002
9	1	30	2	0	19	0.02375	0.02377	0.00002
10	1	30	1	0	19	0.02375	0.02377	0.00002
11	1	30	1	0	21	0.04750	0.04775	0.00025
12	1	30	1	30	21	0.01907	0.01990	0.00083
13	1	30	1	30	21	0.01907	0.01930	0.00023
14	1	30			21	0.03814	0.03830	0.00016
15	1	30	1	30	21	0.05720	0.05740	0.00020
16	1	30	1		21	0.05720	0.05780	0.00060
17	1	30		30	21	0.01907	0.01920	0.00013
18	1	30		30	21	0.01907	0.01920	0.00013

	Time for precipitation. Hrs. Min.		Time of drying. Hrs. Min.		Tempera-ture.	MgO used. Gram.	MgO found. Gram.	Error. Gram.
19	I	30	O	45	21	0.03814	0.03830	0.00016
20	I	30	I	15	21	0.03814	0.03800	0.00014
21	I	30	I	O	21	0.05720	0.05670	0.00050
22	I	30	I	O	21	0.05720	0.05680	0.00040
23	I	30	O	25	65	unknown	0.05650	
24	I	30	O	25	65	unknown	0.05650	
25	I	30	I	15	21	unknown	0.05650	
26	I	O	I	O	21	0.04767	0.04711	0.00056
27	I	O	O	20	59	0.04767	0.04771	0.00004
28	I	O	O	40	{ 62 av. 66 max.	0.04767	0.04671	0.00096
29	I	O	I	O	{ 62 av. 66 max.	0.04767	0.04631	0.00136
30	{ 5 shaking 30 standing } 60				21	0.00095	0.00090	0.00005
31	{ 5 shaking 45 standing } 60				21	0.00048	0.00050	0.00002

Experiments like the above prove the accuracy of the alkalimetric method for magnesia determination. The cases of significant error in the table may be divided into those caused by imperfect removal of the ammonia (Nos. 12 and 16); those caused by drying too long and at too high a temperature in the oven (Nos. 28 and 29); those doubtless caused by imperfect manipulation (Nos. 21, 22, and 26); and, finally, those inherent in the process itself. The latter are all very small if, indeed, they exist at all. Experiments 23, 24, and 25 are comparative only.

Experiments Nos. 30 and 31 show not only the extreme delicacy of the reaction on which the method depends, but they show how rapid the reaction is, even in very dilute solutions, and how insoluble the phosphate is in 10 per cent. ammonia wash.

It was found that five minutes' shaking in a stoppered flask at ordinary temperature sufficed, if followed by fifteen minutes' standing, to completely precipitate any magnesia solution containing as much as 0.002 gram of magnesium oxide in 100 cc. With amounts exceeding 0.05 gram per 100 cc., it is believed that filtration could be begun in five minutes after the end of the shaking process.

In order to ascertain what temperature could be safely used to expedite the expulsion of ammonia from the phosphate precipitates, a series of experiments were made. It was found that

at 55° C. there was no appreciable loss of alkalinity but that at 65° a loss of 1 per cent. had taken place. Several experiments in which the filters and precipitates were removed from the oven as soon as the outer half-inch of the papers were dry, gave identical results with air-drying at 21° C. From fifteen to thirty minutes in the oven at 50° to 60° C. suffices. If the drying of the precipitate proceeds too far, solution in decinormal sulphuric acid is slow. If, however, the drying is stopped at the point described there is enough moisture left so that, on stirring, the precipitate blends quickly with the acid and soon dissolves.

For the drying a large, rectangular, double-walled oven of the kind sold with oil or gas stoves is cheap and convenient.

Unless magnesia determinations are constantly being made, it will often be more convenient to let the precipitates air-dry than to use an oven.

The tendency of magnesia to precipitate with iron and alumina and with calcium oxalate must be met by re-solution in hydrochloric acid and reprecipitation. When the amount of lime is considerable, it is best to burn off the first oxalate precipitate before dissolving in hydrochloric acid. By this means the oxalate is decomposed and the addition of ammonia alone does not cause its sudden reprecipitation. Even in the second precipitation, if the boiling is allowed to proceed longer than is necessary to make the finely crystalline calcium oxalate settle well, some magnesium oxalate is sure to precipitate, betraying its presence by its coarser texture. The solution for magnesia precipitation usually does and always should contain in the form of ammonium chloride the equivalent of 5 cc. of concentrated hydrochloric acid per 100 cc.

THE METHOD.

Add ammonia (sp. gr. 0.90), equivalent to one-tenth of the solution. Cool in water to 20° to 25° C. Precipitate by adding slowly with constant stirring a saturated solution of sodium ammonium phosphate, using 1 cc. for each 0.01 gram magnesium oxide. Stir vigorously for about five minutes or shake in a flask for an equal length of time. In the former case let the solution stand until the clarification of the upper liquid shows that the reaction is complete. In the case of flask precipitations.

if over 0.002 gram of magnesium oxide is present the solution may be filtered in fifteen minutes. Suction may be used if desired but if many solutions are to be filtered at once little is gained by its use. Use 10 per cent. ammonia wash (one part ammonia (sp. gr. 0.90) to nine of water). Deliver it preferably from an aspirator bottle placed about 4 feet above the bench. Wash by decantation as far as possible. Finally wash the precipitate which has gone on the filter, back into the beaker, stir it up with the ammonia wash and bring it again completely on the filter-paper. Wash once more, leaving the upper edge of the filter clear of precipitate so that it can be handled. Avoid assembling all of the precipitate in the apex but leave it fairly evenly distributed over the lower two-thirds of the paper. Allow the precipitates to drain and then transfer each in turn to a dry 5-inch filter-paper, allowing them to remain there open and face upward until the bulk of the moisture has been absorbed. After about three minutes transfer them to fresh dry filters, and in the case of heavy precipitates to a third set a few minutes later. Then place the filters on a shelf to dry at the temperature of the room or place filter-papers and backing on the grating of an air oven having a temperature of 50° to 60° C. After fifteen or twenty minutes in the oven or forty-five minutes in the air, watch for the time when the filters have dried inward half an inch from the margin. This appearance has been found to indicate that the evaporation has gone far enough to insure the expulsion of the free ammonia. The precipitates and filters may then be removed and placed in small dry beakers where they are treated each with a measured excess of decinormal sulphuric acid, and stirred until the papers are disintegrated and the precipitates dissolved. Two drops of a 0.1 per cent. alcoholic solution of methyl orange are then added. If this gives a clear decided pink, enough acid has been added. If it is only faintly pink the excess of acid is slight and some minute particles may have escaped solution. In such cases add five cc. more decinormal sulphuric acid and stir well. Finally dilute to about 100 cc. and titrate back with decinormal sodium hydroxide solution to the appearance of a clear yellow color, free from all suggestion of pink.

1 cc. $\frac{N}{10}$ H_2SO_4 = 0.002 gram MgO.
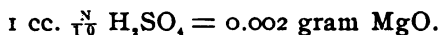
If filtrations have taken place during the latter part of the day the filters may be removed from the funnels and allowed to stand over night after which they are titrated as described.

The writer hopes that the simplicity and accuracy of the method may render it generally useful.

PITTSBURG, December 25, 1899.

A PRELIMINARY COMMUNICATION UPON RICININE.

BY THOMAS EVANS.

TUSON[1] obtained a substance crystallizing in plates which he called ricinine, by extracting castor beans, the seed of the *Ricinus communis*, with boiling water, filtering, evaporating to a thick sirup and again extracting with boiling alcohol.

Tuson states that ricinine is soluble in water and alcohol and very little soluble in ether and benzene, and that when heated with solid potassium hydroxide ricinine evolves ammonia.

He describes, but gives no analyses of crystalline compounds obtained by the action of nitric acid, mercuric chloride, and platinic chloride.

No salts with acids, with the possible exception of the nitric acid salt, were obtained by Tuson.

A few years later Werner[2] claimed that the ricinine of Tuson contained no nitrogen and was the magnesium salt of an acid with the formula $C_{11}H_{20}O_{10}Mg_2.2H_2O$. To this Tuson[3] replied that Werner had evidently investigated an entirely different substance, as his ricinine contained 20.79 per cent. of nitrogen.

Schulze[4] obtained a nitrogenous substance from the germinated seed of *Ricinus communis*, by extracting with alcohol, distilling this off, taking up the residue with water, treating with tannic acid and lead acetate, filtering, removing lead with hydrogen sulphide, and evaporating the filtrate to small bulk.

The impure product was purified by boiling the aqueous solution with animal charcoal and finally by crystallizing from absolute alcohol, from which it separated in small colorless prisms melting at 193° C.

1 *J. Chem. Soc.*, 17, 195.
2 *Jsb. d. Chem.*, 877 (1870).
3 *Ibid.*, 877 (1870).
4 *Ber. d. chem. Ges.*, 30, 2197.

Schulze says he is unable to identify this body with any known substance and calls it ricidine, assigning it the formula $C_{11}H_{11}N_3O_3$.

Pictet[1] gives ricinine the formula $C_{11}H_{18}N_4O_4$ but makes no reference to the original article from which this formula was obtained.

In the following investigation finely ground castor press cake, known as castor pomace, which was kindly furnished by The Brown Oil Co., of St. Louis, was used as a raw material. This was extracted by both Tuson's and Schulze's methods and in each case the same product was obtained, thus identifying the ricidine of Schulze with the ricinine of Tuson.

Tuson's method of extraction was found to be less satisfactory than that of Schulze, although the product so obtained was much lighter in color. It was found advantageous to modify Tuson's process, and use boiling toluene instead of alcohol to extract the residue from the evaporation of the aqueous extract. Upon sudden cooling of the toluene solution ricinine deposits on the sides and bottom of the containing vessel, in small, almost colorless prismatic crystals, which are frequently crossed and sometimes whetstone shaped, and which adhere tightly to the walls of the vessel.

. The ricinine so obtained was purified by recrystallization from alcohol, from which it deposited in small plates frequently united to form rosettes. The melting-point was 193° C. and the analysis gave the following results, which agree very well with Schulze's figures :   .

	Calculated for $C_{12}H_{13}N_3O_3$.	Calculated for $C_{16}H_{16}N_4O_4$.	Calculated for $C_{16}H_{18}N_4O_4$.	Schulze.		Evans.
Carbon	58.30	58.54	58.18	58.20	58.44	58.20
Hydrogen	5.26	4.88	5.45	5.15	5.31	5.06
Nitrogen	17.00	17.07	16.97	17.11	17.15	

In order to render the extraction by Schulze's method more complete a brass extractor of the Soxhlet type was constructed; this held about 900 grams of pomace and was surrounded by a brass jacket, forming an air space between the two, through which the alcohol vapor could ascend to the return condenser, thus keeping the alcohol hot in the extractor. Later on it was found advantageous to place an additional jacket of asbestos around the brass one.

[1] Les Alcaloides vegetaux, 2nd. ed.

The dark brown alcoholic extract was treated according to Schulze's directions, giving a dark brown aqueous solution of ricinine from which yellowish brown crystals deposited on standing for twelve hours or longer.

Further evaporation of the mother-liquor gave a small amount of the substance; it was found impracticable to further concentrate the second mother-liquor, but upon diluting it with water, precipitating with subacetate of lead, filtering, precipitating out the excess of lead with hydrogen sulphide, filtering and evaporating to small bulk, more crystals of ricinine were obtained.   An attempt to remove the brown color of the solution with animal charcoal, either before or after treatment with subacetate of lead, proved unsuccessful.

The impure product was purified by boiling its aqueous solution with animal charcoal.   So prepared the substance showed a melting-point of 193° uncorr., and was evidently the same as the product obtained by the aqueous extraction of the pomace, as both gave the reddish purple color obtained by Schulze[1] by dissolving a few crystals in concentrated nitric acid, evaporating to dryness on the water-bath, taking up with water and again evaporating, and finally adding a drop of ammonia water.

To make sure that the product obtained by the extracting of the castor pomace was the same as Tuson obtained by the extraction of the beans, a quantity of these were extracted by his process and yielded a crystalline substance melting at 193° and was evidently the same as the products already described.

While it was found that neither sample of ricinine gave precipitates with silver nitrate, mercuric nitrate, or mercuric chloride, both gave a feathery crystalline product on long standing of a mixture of cold concentrated solutions of ricinine and mercuric chloride.

The chlorplatinate described by Tuson seems to be due to the presence of some more highly nitrogenous body ; this seems the more probable when we compare Tuson's percentage of nitrogen (20.79 per cent.) with that found by Schulze (17.11 per cent.).

The writer has obtained the chlorplatinate referred to, but in each case it was with a ricinine which was manifestly impure as

[1] *Ber. d. chem. Ges.*, 30, 2198.

it melted partially at 188° and was completely melted at 190°–191°.

Further investigations of the double salt with mercuric chloride, the products obtained by the action of nitric acid and ammonia, are now in progress.

BROMINE DERIVATIVE.

When bromine or bromine water is added to a moderately concentrated solution of ricinine in water, the resultant red solution decolorizes very slowly, and upon heating on the water-bath to drive out the excess of bromine, long colorless radial needles separate, either immediately after the expulsion of the bromine or, if the solution be more dilute, upon evaporation.

The product was purified by repeated crystallization from alcohol, 95 per cent., and upon heating in a capillary tube darkened at 220°–225° C. shrinking at the same time and melted at 229.5°–230° under decomposition and evolution of gas. By moderately rapid heating the melting-point was found at 232°.

Qualitative tests showed the substance to contain both bromine and nitrogen. Upon boiling the aqueous solution with 10 per cent. silver nitrate there was a very slight darkening of the solution but no precipitation of silver bromide, thus showing the substance to be a bromide and not a salt of hydrobromic acid.

The same bromide was obtained upon treating a chloroform solution of ricinine with bromine in chloroform, as follows:

Two grams of ricinine were dissolved in about 200 cc. of chloroform by boiling in a flask connected with a return condenser; to this solution 12 cc. of a solution of 10 cc. of bromine in 50 cc. chloroform was added. After about a minute a considerable precipitate formed and settled to the bottom of the flask. (Ricinine floats on chloroform and it seems probable that the precipitate consists of the hydrobromic acid salt of ricinine, along with some dibromricinine.)

After boiling for ten minutes copious fumes of hydrobromic acid were evolved from the top of the condenser; boiling was continued for some time after these fumes ceased to come off, in all about an hour. The precipitate formed at first did not appreciably increase or diminish during the boiling.

The flask and contents were allowed to stand over night, the precipitate filtered off, washed with chloroform, and the filtrate

evaporated to dryness on the water-bath, the heating being continued until the residue had lost nearly all of its yellow color. The weight of the residue, impure dibromricinine, equaled 2.06 grams, and the dried precipitate weighed 1.82 grams.

When the precipitate was dissolved in boiling alcohol and the solution allowed to cool, prismatic crystals were obtained melting at 192° uncorr., which were evidently unchanged ricinine, as they gave the characteristic reaction with nitric acid and ammonia, while the bromide gave no such reaction.

The weight of ricinine recovered was about 1 gram.

The residue from the evaporation of the chloroform filtrate gave beautiful, long, brittle needles, generally radiating in clusters from several points, and whose length was largely dependent upon the diameter of the beaker and the depth of the solution. These crystals gave the same melting-point, 230° C., as those obtained by brominating in aqueous solution, which would seem to indicate that ricinine was an acid amide or perhaps a diureide. It was at first thought that it might be a substituted uric acid, but the fact that the murexide test fails to give the characteristic color, when performed with potassium chlorate and hydrochloric acid, or with dilute nitric acid, makes this seem doubtful.

The analysis of the recrystallized bromide gave the following results:

Water of crystallization, none.

I. 0.3525 gram substance, dried at 120°, gave 0.5173 gram carbon dioxide, and 0.1084 gram water.

II. The substance was recrystallized from absolute alcohol and 0.2055 gram substance, dried at 120°, gave 0.3000 gram carbon dioxide, and 0.0561 gram water.

	Calculated for $C_{16}H_{14}Br_2N_4O_4$.	Calculated for $C_{10}H_{16}Br_2N_2O_4$.	I.	II.
Carbon	39.53	39.99	40.02	39.81
Hydrogen	2.88	3.27	3.41	3.03
Bromine	32.92	32.79	32.343	....
Nitrogen	11.52	11.42	12.28	11.97

The discrepancy between the results obtained and the theory is probably due to impurity in the form of ricinine. Lack of substance has prevented a more careful separation of the dibromide

from possible impurity; but with more substance more satisfactory results are expected.

The formula $C_{12}H_{11}N_2O$, proposed by Schulze does not suit the bromine derivative as well as the ones suggested above, as $C_{11}H_{11}BrN_2O$, calls for 24.54 per cent. of bromine and $C_{12}H_{11}Br_2N_2O$, for 39.50 per cent.

Ricinine dibromide is soluble in about 200 parts of 93 per cent. alcohol and in practically the same amount of water; it is rather less soluble in chloroform. From dilute solutions in alcohol or water it crystallizes in long needles, while from more concentrated solutions it is obtained as a mass of short, silky, white needles.

So far all attempts to make a bromide containing less bromine have proved unsuccessful, the same product being obtained with varying amounts of bromine.

Ricinine dibromide is soluble in hot, dilute, or concentrated hydrochloric acid and separates out unchanged on cooling. When treated with concentrated nitric acid and ammonia as described under ricinine, it gives no characteristic color.

Its aqueous solution appears to be neutral, and it was found impossible to prepare double salts with platinic or auric chloride.

OXIDATION OF RICININE.

Schulze states that upon oxidizing ricidine with potassium bichromate and sulphuric acid an odor of hydrocyanic acid was obtained, but does not mention other oxidation products.

Upon treatment of an alkaline solution of ricinine with potassium permanganate, the latter was almost immediately reduced, the reduction being accompanied with a faint odor of hydrocyanic acid. Upon filtering off the oxide of manganese a colorless solution was obtained, which became red with a yellow fluorescence upon acidifying with hydrochloric acid; when heated on the water-bath the solution became more intensely colored, and upon evaporation and subsequent cooling, beautiful, long, wavy, salmon-pink needles separated. These proved to be free from inorganic matter and were completely decolorized when their aqueous solution was boiled with animal charcoal.

The oxidation was carried out as follows:

One-half gram ricinine was dissolved in 20 cc. of boiling water

to which 5.5 cc. of approximately normal potassium hydroxide were added. After cooling to 17° C. a solution of potassium permanganate, containing 5.8 grams of the solid in 320 cc. of water, was slowly added until a further addition produced an evolution of a few bubbles of gas; in all 16 cc. of the permanganate were added.

The flask and contents were then allowed to stand for five hours; the oxide of manganese, which had settled, was filtered off after being washed by decantation. The filtrate and washings equaled 100 cc.

The colorless alkaline solution was heated on the water-bath, and made faintly acid with hydrochloric acid, when a few bubbles of carbon dioxide were evolved and the solution became red. Upon evaporation until crystals were deposited on the sides of the dish at the level of the liquid, and then allowing to stand, 0.27 gram of pink silky needles were obtained, melting, after previous blackening, at 269.5°. After repeated boiling of the aqueous solution with animal charcoal, the crystals were obtained snowy white; it was impossible to remove all of the color from the mother-liquor.

The purified substance melted at 279°—280°, becoming black several degrees below the melting-point.

The aqueous solution of the oxidation product is acid to litmus paper, and forms crystalline salts with alkalies as well as with silver nitrate. A test for the degree of acidity, using phenol-phthalein as an indicator, gave the following results:

0.1079 gram acid dissolved in 50 cc. of water required 7.1 cc. standard alkali containing 0.001971 gram NaOH per cc., for neutralization; or 0.00805 gram Na, which equals 7.46 per cent. Na.

The acid contains nitrogen, and on evaporation with nitric acid and moistening with ammonia, gave the reddish purple color characteristic of ricinine, but to a lesser degree,—hence the thought that this may be due to impurity in the form of unoxidized ricinine.

A second portion of 1 gram of ricinine was oxidized in the manner already described, made acid with hydrochloric acid, and concentrated until 6 grams of reddish needles, mixed with dark red prisms, were obtained ; these were filtered off and boiled with benzene for several hours, when a reddish yellow solution

with a green fluorescence was obtained, the prismatic crystals being dissolved while the needle-like crystals appear to be quite insoluble. Upon evaporation of the benzene solutions red prismatic crystals were obtained which became colorless with ammonia, and on evaporation of the solution so obtained gave a colorless crystalline mass.

The difficulty in preparing even small amounts of ricinine has materially interfered with the process of the investigation. The writer is now germinating seed in the dark, and hopes to be able to contribute further in the near future.

UNIVERSITY OF CINCINNATI,
December 29, 1899.

NOTES.

Retention of Moisture by Asbestos.—In the use of the Gooch crucible error may result from ignoring the fact that asbestos (some asbestos at any rate) retains moisture with great tenacity, so that after being dried at 100° C. to constant weight, the Gooch apparatus will suffer a further and notable loss of weight upon ignition over a Bunsen burner.

	Grams.
1. Dried one hour at 100° C., weighed	21.0452
Again dried one hour at 100° C., weighed	21.0450
Then ignited ten minutes, weighed	21.0441
2. Dried one hour at 100° C., weighed	21.0436
Then ignited five minutes, "	21.0429
3. Dried one hour at 100° C., "	21.0418
Again dried one hour at 100° C., weighed	21.0418
Then ignited five minutes, weighed	21.0409
4. Dried two hours at 100° C., "	20.7304
Then ignited one-fourth, weighed	20.7293
5. Dried three hours at 103° C., weighed.	20.8250
Then ignited one-fourth hour, weighed	20.8246
6. Not dried in air-bath	......
Ignited five minutes	21.0950
Then ignited again one hour	21.0944
7. Asbestos in larger quantity from a Hirsch funnel dried in a platinum crucible six hours at 90°–100° C.	20.2828
Then ignited one hour	20.2811
8. Ignited in a platinum boat in porcelain combustion tube in current of oxygen, then dried three hours at 100° C	21.1742
Then ignited one hour	21.1726

The asbestos used in these experiments was, of course, previously ignited and purified.

It is therefore necessary, when the weight of a dried precipitate is to be found, either to get the preliminary weight of the Gooch crucible by drying the same length of time, and at the same temperature as is intended with the precipitate; or much more conveniently, to find, once for all, the weight of the moisture retained by the dried Gooch crucible, and make the necessary correction when getting weights of precipitates.

GEORGE AUCHY.

The Determination of Graphite by Loss.—The figures given in the above note show that it is necessary to observe precaution in determining graphite in pig iron by the method of loss upon ignition, if the operator prefers the use of asbestos to that of a weighed paper disk or to counterpoised filters. Although the proposers of this method of determining graphite (Eggertz, Tamm, Crobaugh, Dougherty, Rodgars) are unanimous in directing the use of weighed paper for filtering, asbestos seems preferable for the reason that by its use the time and labor of drying and weighing the paper disk, or of drying and counterpoising the filters, is saved. With asbestos no weight is taken except that of the Gooch crucible plus graphite, etc., after drying, and again after ignition, the loss representing graphite. In the absence of a Gooch crucible the filtration may be made in a Hirsch funnel, or a Shimer funnel, and the asbestos and graphite then transferred to an ordinary crucible with the graphite part of the asbestos pressed against the wall of the crucible, as is also done when a Gooch crucible is used.

In using this method of loss upon ignition (filtering through counterpoised filters) Crobaugh obtained somewhat variable results (3.53 per cent. to 3.75 per cent.) which he attributed chiefly to non-homogeneity of the drillings. The presence of hydrated silica could not serve as an explanation, because the elimination of the silica by the addition of hydrofluoric acid during solution of the drillings, is a distinguishing feature of his method. The writer of this note also obtained varying results by the method, which, in his opinion were due, not to any lack of homogeneity in the drillings (mixed as they were by the aid of alcohol as recommended and found necessary by Shimer), nor

to the presence of gelatinous silica not completely dehydrated by the heat used in drying the graphite (Drown being strictly followed in dissolving the drillings as in phosphorus determinations), but probably to the fact that graphite thus obtained is not always pure carbon, but contains sometimes other combustible matter—combinations of hydrogen, oxygen, nitrogen, and sulphur in some form. For smaller percentages the method may serve. By combustion as usual, we obtain 3.21 per cent., 3.24 per cent ; by loss upon ignition, 3.35 per cent., 3.36 per cent., 3.38 per cent., 3.20 per cent.

That gelatinous silica, if present, is not dehydrated by the drying of the graphite, was found by Tamm. An experiment by the writer showed 0.0094 gram water retained by about 0.13 gram gelatinous silica after being dried as graphite is dried.

<div align="right">GEORGE AUCHY.</div>

The Persulphates of Rubidium, Cesium, and Thallium.—In the October part of this Journal,[1] there is a short paper by Foster and Smith on the above subject. As I have recently prepared and partially investigated these salts, I consider it advisable to publish the present note, retaining details for a paper to be published later.

The rubidium and cesium salts were prepared from ammonium persulphate by double decomposition, purified, and recrystallized. The crystals are not isomorphous with those of the potassium salt (triclinic), but with those of the ammonium salt (monoclinic). As mixtures of the potassium salt with the others have been obtained in well-formed monoclinic crystals, notwithstanding a great preponderance of potassium salt, it is evident that we have here to deal with an isodimorphous group.

The thallous salt has not yet been obtained pure, but mixtures of it with ammonium persulphate have been obtained in crystals isomorphous with the above monoclinic group. As the electrolysis of thallous sulphate solution would present interesting peculiarities, owing to the existence of thallic compounds, it was decided to investigate that subject also. It was found necessary to delay this, however, to permit of a preliminary investigation of thallic sulphate and its double salts, which is at present being carried out. Thallous persulphate, $Tl'_2S_2O_n$, is isomeric with thallous thallic sulphate, $Tl'Tl'''(SO_4)_2$ or $Tl_2SO_4Tl_2(SO_4)_2$.

UNIVERSITY OF EDINBURGH,
October, 1899.
<div align="right">HUGH MARSHALL.</div>

1 This Journal, 21, 934 (1899).

OBITUARY.

SIR EDWARD FRANKLAND.

WE are again called upon to note the departure of a co-
worker and master in our chosen field of science. Eulogy
is not necessary. The good he has achieved lives after
him, and we would merely note that the researches of Sir Edward
Frankland, extending over a period of thirty years, relate to
work in pure, applied, and physical chemistry. Those in pure
chemistry were conducted at first in the laboratories of Playfair,
Bunsen, and Liebig. They include subjects related to each other
as follows: the conversion of the cyanogen group into the carboxyl
group; the change of the alkyl cyanides to the corresponding
organic acids, the saponification of ethyl cyanide was
announced by Edward Frankland and Hermann Kolbe when
they were fellow assistants in Playfair's laboratory in 1845.
Although this reaction was not then pursued beyond the mono-
basic acids, others applied it successfully in other directions
Then followed the action of metallic potassium upon ethy
cyanide and the polymerization of the latter, the isolation of the
organic radicals, and the discovery of the organo-metallic com-
pounds. Of these, which were investigated by Frankland
throughout his scientific career, were zinc methyl and zinc ethyl,
in the study of which the author remarks: '' I had not pro-
ceeded far in the investigation of these compounds before the facts
brought to light began to impress upon me the existence of a
fixity in the maximum combining value or capacity of saturation
in the metallic elements which had never before been suspected.''
The ready introduction of negative chlorine into bodies for a
more electropositive constituent is a fact to which we give little
thought. ''The inverse process'' in the day of Frankland
''had been successfully accomplished in comparatively few
cases.'' Through zinc methyl he succeeded in substituting
methyl, ethyl, etc., for electronegative constituents, thus
''opening up a most extensive and absolutely new field of research.''

Next came the syntheses of acids of the lactic series, of the
acrylic series (aiming here to produce the higher fat acids by
direct synthesis from acetic acid), with the formation of
ethers and ketones.

In applied chemistry Frankland studied the ''hydrocarbon''
process of gas-making and contributed much to the knowledge
of gas manufacture. He also studied magnesium as a source
of light.

In connection with his studies of the water supply of London he developed new and accurate methods for the determination of the amount of organic carbon and nitrogen in potable waters. As a member of the Royal Commission on the Pollution of Rivers he conducted, during a series of years, most exhaustive researches upon the question of water supply. Frankland also gave attention to the spectra of gases and inquired into the source of muscular power. He presented four or five papers relating to "climate," discussing the physical cause of the glacial epoch. Crooke's radiometer and colored solar halos also engaged his earnest thought.

The preceding lines indicate in a measure the scientific activity of the great investigator whose earthly career ceased on August 9, 1899, at the age of seventy-four years.

WM. A. NOYES,
A. B. PRESCOTT,
EDGAR F. SMITH,
Committee.

NEW BOOKS.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By H. MEYER. Authorized translation by J. BISHOP TINGLE. New York: John Wiley and Sons. London: Chapman and Hall. ix + 133 pp. 12mo. Cloth. Price, $1.00.

This book is a translation of the original German edition with various corrections, additions, and changes in arrangement made partly by the author and partly by the translator. The successful methods known at present for the determination of organic radicals have been collected in the five chapters of this little volume, which deal with the following topics: Chapter I.—Determination of hydroxyl; Chapter II.—Determination of methoxyl, ethoxyl, and carboxyl; Chapter III.—Determination of carbonyl; Chapter IV.—Determination of the amino, nitrile, amide, imide, methyl imide, and ethyl imide groups; Chapter V.—Determination of the diazo group, the hydrazo radical, the nitro group, the iodoso group, the iodoxy group, the peroxide group, the iodine number.

The book contains then in compact form much valuable material that the student must ordinarily gather from various texts and periodicals. References to original articles are given. The improvements and additions have brought the book up to date. The translator has done his work in a commendable way. The excellent work of the publishers is too well-known to require further comment. LOUIS KAHLENBERG.
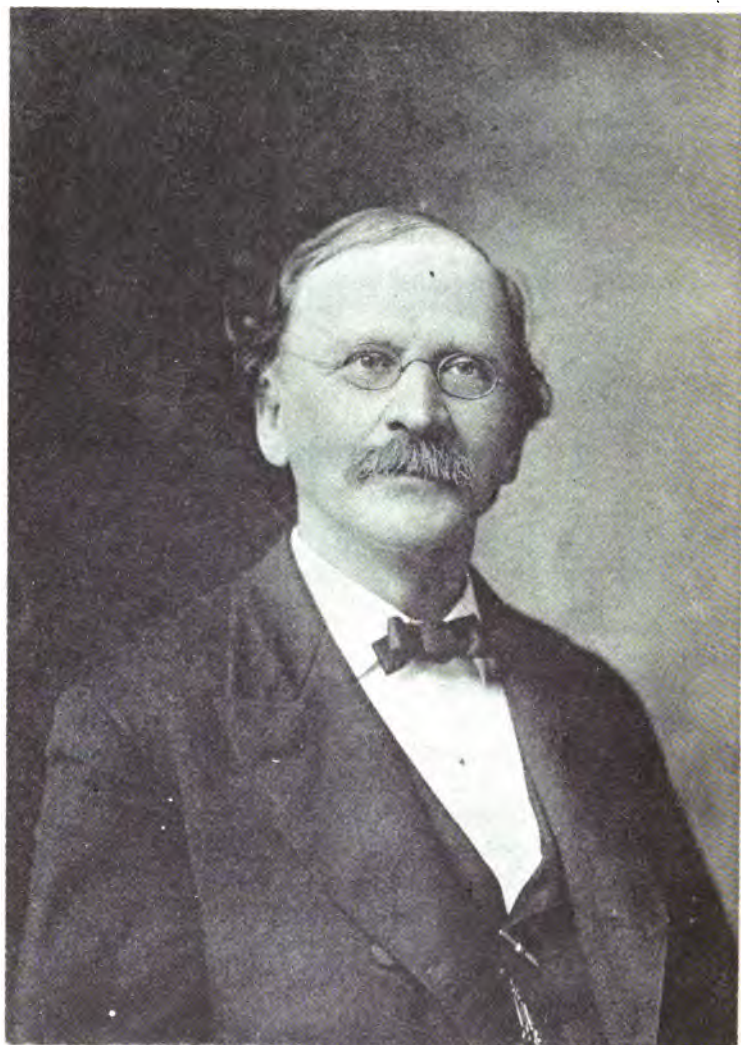
Edward W. Morley.

THE JOURNAL

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ARE FURTHER EXPERIMENTS NEEDED FOR DETERMINING THE ATOMIC WEIGHT OF OXYGEN?

BY EDWARD W. MORLEY.

THE precision of experiments on the atomic weight of oxygen has been gradually so much increased that, in some cases, the mean error of a single determination is less than 1 part in 10,000. The agreement of different series of experiments is not so good, but if the work of different experimenters agreed well, the question, how accurately do we really know the atomic weight of oxygen, is not one which we can readily answer. Neither the concordance of the experiments of a given series, nor the agreement of the results of series of experiments by different observers, can excuse us from search for sources of error. All sciences which have to do with measurement afford sufficient instances of the fact that our conclusions are to be received with a certain suspense of judgment. And chemistry well illustrates that he is wise whose assertions regard the possibility of finding at some time evidence to the contrary.

The history of experiment on the atomic weight of oxygen affords an interesting example of the fact that neither the con-

cordance of individual observations nor the agreement of differ-
ent experimenters proves that a measurement is right.   Toward
the middle of the century, Dumas made his classic experiments
on the composition of water.   The probable error of a single
experiment was, in round numbers, 1 part in 400, so that the
probable error of the average of the 19 famous experiments
was 1 part in 2250.   Now, this means that his final value was
not likely to differ more than a certain small quantity from the
result of the repetition of even a very large number of experi-
ments made in the same way, with the same skill and care.·   But
as to the difference between this result of the 19 experiments and
the unknown true value, we are told absolutely nothing by the
proposition that the probable error of Dumas' result was 1 part
in 2250.   It is a commonplace to say, that the calculation of the
probable error of a series of experiments does not show how
nearly the result approaches the truth, but how near it is to the
result of a greater number of similar experiments.   It decides,
not how nearly we approach the desired goal, but whether it is
useful to persevere by the present method of approach.   Dumas
made 19 observations, and got the value, 15.96, with a probable
error of 0.007 ; that is, if he had made 100 or 1000 experiments,
it is unlikely that the final result would not have been between
15.95 and 15.97, and very unlikely indeed that it would not have
been between 15.94 and 15.98.   But he would never have
obtained a value near that which now commands confidence.

It is interesting to recall that there is hardly any instance on
record where the judgment of an experimenter as to the degree
of approximation to the truth attained in his work has been bet-
ter justified than in the case of Dumas' classic experiments.   As
we all remember, towards the end of his work, there was discov-
ered in his own laboratory a source of error, not easy to elimi-
nate, which had affected all his determinations.   The amount of
the error was not a fixed quantity, and no numerical correction
could be applied to the results of observation.   Dumas accord-
ingly gave to the public the uncorrected and unmodified results
of experiment.   But he also stated his opinion as to the degree
in which his results approximated, not to the mean of a larger
number of experiments of the same kind, but to the unknown
and unattainable true value.   He expressed the hope that his

value would be found not more than one part in 200 from the
result of those subsequent experiments which should be thought
satisfactory ; and it is by just 1 part in 200 that his value differs
from that which is now accepted.

So the concordance of Dumas' experiments did not prove that
his result was right; neither did the agreement of experiments
by different observers. Erdmann and Marchand made eight exper-
iments by a method like that of Dumas, with some modifications.
Their result was 15.973, with a probable error of 0.011. This
value differs from that of Dumas by less than the sum of the
probable errors, so that that agreement is perfectly satisfactory. '
So, also, Regnault determined the ratio of the densities of oxy-
gen and hydrogen, from which was computed the atomic weight
of oxygen as 15.963, with a probable error of 0.004. The
results of Dumas, of Erdmann and Marchand, and of Regnault,
show a very good agreement. But all of them, and the mean of
all of them, we now know to be in error by 1 part in 200.

I adduce this example, somewhat in detail, to enforce the
proposition that we must not excuse ourselves from looking for
error because observations agree. We have experiments which
give the atomic weight of oxygen with a probable error of 1 part
in 50,000, but do we know it within 1 part in 1,000? Each
individual experimenter whose work would now be regarded as
free from known and tangible error, agrees fairly well with the
mean of all. For instance, Noyes' results show that degree of
concordance which would justify us in expecting that, if he
were to make 100 or 1,000 experiments, his final mean would be
as likely as not to be larger or smaller by 1 part in 9,500, and
his result differs from that which we accept by 1 part in 900.
So Cooke and Richards assign a value which is just as likely as
not to be within 1 part in 8,000 of the result which they would
have obtained by multiplying observations ; and it differs from
that which we accept by 1 part in 1,500. But do we know that
their means, and the means of all published results taken to-
gether, are not in error by 1 part in 900? The concordance of
the results of a single experimenter, and the agreement of differ-
ent experimenters, does not justify us in asserting that we do.

In determining the atomic weight of oxygen, it has been
somewhat difficult to determine directly all three of the quanti-

ties involved, and so to make what Stas called a *complete* synthesis. Berzelius, Dumas, and Erdmann and Marchand, weighed oxygen and weighed water, thus determining hydrogen by difference. More recently, Dittmar and Henderson, and Leduc used the same method. Cooke and Richards, and Keiser, weighed hydrogen and weighed water, while Rayleigh and Noyes weighed hydrogen and weighed oxygen. Any proceeding which weighs hydrogen directly has a great advantage in precision; different determinations in a given series agree better among themselves, and the series of different experimenters also agree better. But there is also a second, more important advantage. We have reason to believe that the constant errors involved in weighing hydrogen are small, for it is possible to obtain hydrogen with less than $\frac{1}{10.000}$ or even $\frac{1}{20.000}$ of its weight of impurity. There is no difficulty in weighing oxygen or water with accuracy, so if we weigh hydrogen and also weigh either oxygen or water, we may hope for a near approximation to the true value of the ratio sought.

We may hope, but we cannot *know*. We may believe that our hydrogen is pure, and that there was no error through leakage. But an unsafe stop-cock might make the apparent weight of the hydrogen in a series of experiments seem always smaller than the fact, and might yet leave the individual experiments so concordant with each other as to seem trustworthy.

If, however, we can weigh hydrogen and can weigh oxygen, and then combine them and weigh the water produced, we can at least give a better reason for our hope, if we find that the product is nearly equal to the sum of the components. The manipulation in this case is costly, and is so difficult, and involves so many minute details, that not many have patience and time sufficient for it, so that no great number of such complete syntheses has been made, and these few were made in conditions but little varied. When such complete syntheses shall have been made by different observers, with those variations of apparatus and method which may seem wise to them, we shall be able to judge of the magnitude of the errors to be feared. If such results are not concordant, we shall have much to learn as to sources of error; but we now see some reason to expect that they will not be discordant. However, even if they are not dis-

cordant, we are not to excuse ourselves from further study of sources of error.

Before repeating determinations so troublesome, and before studying unknown sources of errors not yet detected, the experi- . menter should receive all possible assistance from chemical theory and from criticism. For some that criticism may be most profitable which is friendly and sympathetic ; but, for the experimenter, the value of the criticism depends on the knowledge and the acuteness of the critic. Dr. Hinrichs published, some five years ago, a criticism of all determinations and computations of atomic weights since Dumas. As is well known, he is a most strenuous and insistent supporter of Prout's hypothesis. Looking hastily through the volume, there was found, towards the end, evidence that its author was one of those who, some thirty years ago, discerned that which, in the hands of Mendeléeff, became the periodic law. It seemed possible that one who had early seen some indications of this law might, perhaps, also have discerned, even if obscurely, some principle relating to atomic weights. I therefore once spent some time and pains in carefully reading the book, and considered at length those passages, which, if any, contained valid criticism of the views which are generally accepted.

Hinrichs believes that the mean of a series of determinations of an atomic weight cannot give the true value sought. This proposition he deduces from a mathematical discussion. He believes that as larger and larger quantities are taken in our analytical operations, the results differ regularly from ideal accuracy ; sometimes the difference continually increases as the quantity taken increases; sometimes the difference increases to a maximum and then decreases again. The proper computation of an atomic weight then, according to Hinrichs, consists not in taking the mean of different observations, made with different weight of materials, but in determining the limit towards which the series converges as the weight taken decreases. A good illustration is given : we cannot determine the weight of a new coin by weighing any number of old coins ; every coin is worn and therefore light, and the mean weight of any number whatever is therefore necessarily below the mean weight of new coins. But if we weigh old coins and note the date of each, we may

take the mean weights for each year separately.   If we examine
coins enough, these means when plotted as the ordinates with
the years as the abscissas, will give us a "fairly regular curve,
lowest for the oldest coins, gradually rising towards a *limit*
which they would not quite reach.   This higher limit would
evidently be the mean weight of the new coin."

This is an intelligible proposition.   It seemed to me worth
while to examine it, for to this proposition one of the most
enthusiastic and most active supporters of Prout's hypothesis, a
man not lacking in shrewdness or ability or learning, has
entrusted the defense of his favorite belief.

He asserts that an atomic weight as determined by experiment
is variable, that it depends on the amount of substance taken for
the analysis or other operation, and that it varies in a continuous
and regular manner.   His proposition is, that an atomic weight
as determined by experiment is a function of the weight of sub-
stance taken.   Is there any evidence in favor of it ?

I answer, first: Theory does not afford any evidence for it.
Hinrichs deduces this proposition from theory by a discussion
which is mathematical in form.   Whether the proof is sound
need not be considered, for his theory does not attempt to show
the order of magnitude of the regular and continuous variations
which are affirmed to depend on the weight of substance taken,
and to show whether they can be separated from the irregular
and discontinuous errors due to accident.   We are sure that
accidental errors exist ; we may concede, for argument, that
regular and continuous variations also exist ; but this is far from
implying that the actual errors in a given set of experiments
will be largely or even perceptibly of the latter kind.   Theory
shows that there is a diurnal tide in the atmosphere ; but theory
does not show that the differences noted in a series of ten obser-
vations of the barometer at different hours of the day will follow
the law of the diurnal tide.

But, secondly : Facts do not agree with the proposition.   The
accidental errors of the most precise experiments yet made are
so much greater than any *systematic* variations, that nothing but
accidental variations can be detected.   To prove this, let us
consider Stas' synthesis of silver nitrate from pure silver.   This
is one of the most important determinations ever made ; Hin-

richs has discussed it twice in his volume ; he asserts that the ratio of silver nitrate to silver found in each analysis depends on the weight of silver taken, and twice draws curves to show this. I assert, on the contrary, that the errors, which average only 1 part in 40,000, are purely accidental, and that they follow no law.   This can be proved by proving that the ratios obtained depend on any other quantities selected by accident just as much as they depend on the weights of silver taken.   Hinrichs plots the results of the ten determinations, using for abscissas the weights of silver taken, and so obtains tolerable curves.   I plotted the same ten observations, using for abscissas not the weights of silver taken but ten numbers selected by *sortes Virgilianae*, and get curves quite as tolerable as before ; and this I did with ten different sets of abscissas, all selected by pure accident. Now, quantities which depend on any one of eleven sets of abscissas, ten of which are selected by accident, are themselves accidental in their variations, and the variations follow no law.   So far as the facts are examined, they give no evidence in favor of Hinrichs' proposition ; we have seen that theory is equally chary of her support, and we may safely dismiss the suspicion that any source of systematic error can be detected in deducing atomic weights from the means of good experiments.

Within the limits of convenience, it is well to vary the amount of substance taken in analytical determinations.   This has been a frequent practice in the finest investigations.   But that this practice derives any support from the so-called "limit method" cannot be conceded.

This criticism, this attempt at a theory, then, removes no obstacles and reveals no threatening pitfalls.   If we desire a firmer foundation for our system of atomic weights, we must simply enlarge the experimental basis of our knowledge.

If it is only by further experiment that we can make surer of the atomic weight of oxygen, we are to consider what kind of experiments is most desirable.   It is chiefly for the sake of eliciting discussion on this point that the subject of this address has been chosen.

Our present value for the ratio between oxygen and hydrogen rests on one single chemical combination, and upon two processes for determination.   The first is, the synthesis of water from its

components. The second is, the determination of the densities of the gases and of their volumetric ratio. Let us consider these in order.

What synthetic experiments should be repeated? We are met by the fact that a complete synthesis, in which hydrogen and oxygen and water are all three weighed, can be made with errors only about one-fourth as large as the errors in any of the syntheses where only two substances are weighed out of the three concerned. Other things being equal, then, this process is by far the most promising. But, so far it has been carried out adequately by only one experimenter. Conditions were varied somewhat, it is true, but by no means so much as they would be varied if the same person repeated the experiments after an interval of years; by no means so much as if others were to undertake such complete syntheses. Lately, Keiser has devised a process which varies in many particulars from that already executed; it is very desirable that he should make a series of experiments, after adequate study of sources of error and of means of avoiding them. It is also desirable that, if possible, the original process of complete synthesis should be repeated with the little modifications which time is sure to introduce. These two would be enough, as far as synthesis is concerned; unless, indeed, through the invention of another process by a third experimenter, we could have still more. Other syntheses of water than by a *complete* synthesis seem less likely to be of much service, except as a school of experimentation.

What further work is desirable on the ratio of densities and of combining volumes of hydrogen and oxygen? Three constants are involved: the density of oxygen, the density of hydrogen, and the volumetric ratio.

The density of oxygen is known with a probable error of about 1 part in 50,000. It is very probable that no number whatever of further determinations would change this value by 1 part in 10,000. No further work upon this density seems at present desirable, except that whoever determines the density of hydrogen cannot well fail to determine that of oxygen also.

The density of hydrogen demands further experiment. It is possible to make, by some one of three or four slightly different processes, a series of experiments whose average variation shall

be less than 1 part in 3,000, or 5,000, or even 10,000; but different series do not agree sufficiently with each other.   We are far from knowing the density of hydrogen so well that more observations might not change our value by 1 part in 2,000 or 3,000.   It is very desirable that further observations should be undertaken by at least two different methods.   In one method, hydrogen should be weighed while absorbed in palladium, should be then transferred to a measuring apparatus without the use of stop-cocks, and should be there measured.   This process should be repeated with measuring apparatus of varied volumes.   In another method, hydrogen should be weighed after Regnault's method, in a counterpoised globe, but with such precautions that leakage through a stop-cock, and contamination with vapor of mercury; should be excluded.   The globe should be exhausted till the remaining air is a small fraction of a millionth, should be sealed off from the pump, and should be connected with a condenser at the temperature of liquid air, so as to remove mercurial vapor.   After this hydrogen is to be admitted without the use of stop-cocks.   The manipulation is not difficult, and the method would confirm the results of the previous method.

The ratio of the combining volumes of hydrogen and oxygen is not known with the degree of confidence which is desirable. The history of the matter is not an interesting one.   Further continuance of the two series of experiments on which the present value depends would be most unlikely to change it by 1 part in 10,000, for its probable error is 1 part in 40,000.   But one of the experimenters has obtained results differing from that finally adopted by as much as 1 part in 220.   The other experimenter has entirely discarded the result of one series and replaced it, not by a better series of the same kind but by one of a quite different nature, not carried to its proper completion, and accordingly reduced by the use of the constants of van der Waals' equation.   It is desirable that experiments be made to furnish means for a new reduction by measuring the change of volume when 2 volumes of hydrogen and 1 volume of oxygen are mixed, being at the same pressure before and after mixing.   This experiment has lately been made by Berthelot, whether with sufficient precision for the purpose is not known at this moment. It is also desirable that the ratio of the combining volumes of

oxygen and hydrogen should be measured with the gases contained in vessels of the dimensions of those used for obtaining their densities.

If these syntheses and these studies of ratios of densities and combining volumes should agree as well as it is safe to expect, we should know the atomic weight of oxygen as confidently as we can know it while the value rests on a single chemical process, the combination of the two gases to form water.

But this is not so much as is desirable. We know the atomic ratio between silver and oxygen with considerable confidence, because this rests not on a single chemical process but on eight different chemical processes, which give eight independent results, and because these eight results agree. Is there, then, any chemical process by which the atomic ratio of oxygen and hydrogen can be determined, other than the analysis or synthesis of water? Is there any element whose atomic ratio to oxygen is well known, whose ratio to hydrogen is capable of accurate direct determination?

It is probable that, given an adequate equipment, the direct ratio of hydrogen to chlorine, of hydrogen to sodium, of hydrogen to magnesium, or of hydrogen to aluminum, could be determined with sufficient precision for the purpose, provided that the ratio of chlorine to oxygen, of sodium to oxygen, of magnesium to oxygen, and of aluminum to oxygen are well enough known. This may not now be the case with aluminum or magnesium, but is the case with chlorine and with sodium, whose atomic ratios to oxygen may be fairly assumed to be known within 1 part in 2,500. If, now, we can determine the ratio of chlorine to hydrogen, or of sodium to hydrogen, to 1 part in 5,000, we could compute, by a new method, the ratio between hydrogen and oxygen. If this should agree with the present value, within some such quantity as 1 part in 2,000, we should be as confident of the truth of our value of the atomic weight of oxygen as we can well hope to be.

The difficulties in making a complete synthesis of hydrochloric acid are not small, nor are they all well understood. Some unexpected circumstance may be prohibitive. But there is good reason to hope that 3 or 4 or 5 grams of hydrogen could be

weighed, that a nearly equivalent quantity of chlorine could also be weighed, that the two could be combined, and that the product could be weighed.   One serious difficulty would be found in attempting to prepare pure chlorine, but the difficulty does not seem insuperable.   The manipulation of the corrosive element requires invention, but seems not difficult.   For the collection of the hydrochloric acid in a weighable form, there seem to be alternative methods, not very troublesome of execution, unless unforeseen difficulties are encountered.   If the ratio between hydrogen and chlorine could be determined to 1 part in 5,000 or to 1 part in 10,000, it would be a very interesting addition to our list of known constants, most helpful in establishing confidence in the ratio between oxygen and hydrogen.

So, also, if sodium can be prepared of sufficient purity, or of sufficiently constant impurity, it seems possible to weigh 100 or 200 grams, to act on it with water in such a way as to produce a slow evolution of hydrogen, and to determine the weight of this hydrogen by loss.   Whether sodium can be obtained sufficiently free from absorbed hydrogen and whether it can be prepared for weighing without attacking the vessels which contain it, are questions which need further experiment.   It is probable that a vessel of platinum-iridium alloy could be made which would make success almost certain, but at considerable cost.   In this case also, if the ratio between sodium and hydrogen can be determined to 1 part in 5,000, or 1 part in 10,000, the result would inspire confidence, or, if it must be, distrust, in our present value for the ratio between oxygen and hydrogen.

These suggestions, necessarily tentative in their nature, are submitted to the American Chemical Society, in the hope of obtaining from those who do me the honor to listen to them or to read them, expressions as to the desirability of making experiment in the lines described, and discussions of the new methods indicated as possible.

A PRELIMINARY STUDY OF THE COBALTICYANIDES.

BY E. H. MILLER AND J. A. MATHEWS.

S EVERAL years ago during the course of an investigation of the ferrocyanides of zinc and manganese,[1] it was suggested that a study of the reactions between potassium cobalticyanide and solutions of metallic salts might be of interest and that, possibly, this compound might be found useful as a reagent in either qualitative or quantitative analysis. A careful search through the literature showed that the subject had not been thoroughly investigated; that the cobalticyanides of many metals were unknown and that the properties, especially the solubilities, of the known cobalticyanides were but incompletely recorded. Apparently no work has been done on these compounds for many years, while most of the investigations bear dates prior to 1857.

The general procedure adopted in this work was:

First.—To try the action of a half-normal solution of potassium cobalticyanide[2] on half-normal solutions of all the common metals. They were first added to each other in equal quantities and the filtrate tested to see which reagent was in excess; and, having found the amount of potassium cobalticyanide needed to precipitate a given metal, to work in subsequent experiments with quantities which gave a slight excess of the precipitant. Although these solutions were only approximately half-normal, they were made with sufficient care to distinguish in the resulting precipitates between a normal cobalticyanide and a double potassium-metallic cobalticyanide. The indications show that in nearly every case a normal salt is produced by a reaction of simple double decomposition.

Second.—The solubility of the precipitates so obtained was tested in every instance in nitric, hydrochloric, sulphuric, acetic, and oxalic acids, in ammonium hydroxide and caustic potash; in all cases both cold and hot.

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1 This Journal, 19 547 (1897).

2 Based on the hydrogen equivalent in grams per liter.

These tests were made by adding the acid or alkali to the original liquid containing the precipitate, and, in each instance, an amount of solvent equal in volume to the original liquid was employed. A few precipitates were filtered and their solubilities tested in concentrated acids.

The special solutions used were of the following strengths:

$K_3Co(CN)_6$(N/2) 55.52 grams per liter.

HNO_3	(1 : 3)	sp. gr.	1.135 = 22 per cent.	
HCl	(1 : 1)	" "	1.10 = 20 " "	
H_2SO_4	(1 : 4)	" "	1.20 = 28 " "	
$HC_2H_3O_2$		" "	1.03 = 22 " "	
$H_2C_2O_4$	saturated solution		= 10± " "	
NH_4OH	(1 : 2)	sp. gr.	0.96 = 10 " " NH_3.	
KOH		" "	1.11 = 10 " " K_2O.	

No highly colored or characteristic precipitates have as yet been found which can be employed as indicators to show an excess of potassium cobalticyanide, nor do the precipitates settle readily enough to allow this point to be determined by cautious additions of cobalticyanide to the clear supernatant liquid or by spot tests. In every precipitation the potassium cobalticyanide was added to the metallic salt solution and the presence of either substance in excess had usually to be determined in a few drops of the filtrate from the resulting precipitate. The experimental part of our work will show that, in general, the cobalticyanides insoluble in water, are also insoluble in and unaffected by acids, but are soluble in or decomposed by alkalies. None of them are decomposed by boiling as is the case with several ferricyanides. There is little similarity in either solubility or appearance between the corresponding ferri- and cobalticyanides. The metals except those of the alkalies and alkaline earths were taken up in their qualitative sequence, beginning with the silver-lead-mercury group.

Silver Cobalticyanide.—When equal volumes of half-normal silver nitrate and potassium cobalticyanide solutions are mixed, the silver is completely precipitated as silver cobalticyanide, a white curdy precipitate, which settles and filters well; is insoluble in all the acids used, being transposed by hydrochloric acid; is soluble in ammonia and decomposed by potassium hydroxide giving a precipitate consisting mostly of silver oxide.

Lead Cobalticyanide.—Neither lead acetate nor nitrate are precipitated by potassium cobalticyanide, either in neutral or acid solutions. Zwenger[1] made it from lead carbonate and cobalticyanhydric acid. This salt, crystallizing in laminated crystals containing 4 molecules of water, he says, is soluble in about 3 parts of water from which solution it is precipitated by ammonia as a basic salt.

Mercurous Cobalticyanide.—Mercurous nitrate gives with potassium cobalticyanide a white, flocculent precipitate, which settles quickly. It was therefore possible to use concentrated ammonia as an indicator. Spot tests on porcelain showed a black precipitate as long as there was an excess of mercurous nitrate. Mercurous cobalticyanide is transposed by hydrochloric acid and seems to be partly changed by hot sulphuric acid but not by oxalic acid. It is unaffected by nitric and acetic acids, but decomposed by alkalies. Mercurous cobalticyanide is probably a normal salt, having the formula, $Hg_3Co(CN)_6$.

Mercuric Cobalticyanide is unknown. There is no precipitate formed when potassium cobalticyanide is added to mercuric chloride either in neutral or acid solution.

Arsenic, in hydrochloric, sulphuric, or ammoniacal solution gives no precipitate.

Antimony in a solution sufficiently acid to prevent the precipitation of a basic salt, gives no precipitate.

Stannous salts in neutral, acid, or potassium hydroxide solution are not precipitated by potassium cobalticyanide. Gmelin[2] states that stannous but not stannic salts are precipitated, but does not give the conditions under which he obtained the precipitation.

Cupric Cobalticyanide.—When a solution of copper sulphate is completely precipitated by potassium cobalticyanide solution, there results a turquoise-blue compound. This salt, apparently $Cu_3Co_2(CN)_{12}$, is insoluble in all acids, cold or hot; very soluble in ammonia, and with caustic potash it turns green, becoming darker and darker until black cupric oxide separates. The ammoniacal solution upon evaporation gives small shining blue crystals to which Zwenger,[3] who first worked with this

1 *Ann. Chem.* (Liebig), **62**, 158.
2 "Handbook of Chemistry" (1852), Vol. VII, p. 495.
3 *Loc. cit.*

compound, assigns the formula $Cu_3Co_2(CN)_{12} . 2NH_3 . 5H_2O$.

Cuprous Cobalticyanide, of which no mention is found in the literature, results from the precipitation of cuprous chloride by means of potassium cobalticyanide. It is a faintly yellow precipitate which filters badly; it is insoluble in acids and cold ammonia but soluble in hot, dilute ammonia. It is partly decomposed by potassium hydroxide in the cold and completely when hot. It is slowly oxidized by nitric acid, giving the blue cupric cobalticyanide.

Bismuth Cobalticyanide.—A solution of bismuth nitrate, rather strongly acid with nitric acid, is precipitated by potassium cobalticyanide giving a dense white precipitate, very soluble in hydrochloric but insoluble in the other acids and ammonia. Potassium hydroxide gives in the cold $Bi(OH)_3$, which, on boiling, may be changed to yellow Bi_2O_3. The original precipitate seems to be a normal cobalticyanide, but it has not yet been analyzed and no mention of such a compound was found in the literature.

Cadmium Cobalticyanide.—The statement appears in Gmelin's "Chemistry" (1852) that with cadmium sulphate, potassium cobalticyanide forms a brown precipitate, turning white later, soluble in excess of cobalticyanide and also in acids. In our experiments cadmium chloride was employed; the precipitate was white and amorphous, not soluble in excess of cobalticyanide nor in any acid except warm hydrochloric acid, from which it reprecipitates on cooling. To determine whether it is changed or not during this treatment will require quantitative work. It is completely soluble in cold ammonia but potassium hydroxide decomposes it, giving cadmium hydroxide.

Solutions of gold, platinum, titanium, vanadium, uranium, or zirconium are not precipitated by potassium cobalticyanide.

Aluminum chloride and chromium salts gave no precipitate with cobalticyanide. Certain double ammonio-chromic cobalticyanides have been described by Christensen[1] and by Braun.[2]

Ferric Cobalticyanide.—When potassium cobalticyanide is added to a solution of ferric chloride no precipitate forms at first, but the solution assumes a light green tint and on standing a

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[1] *J. prakt. Chem.* [2], 23, 52.   [2] *Ann. Chem.* (Liebig), 125, 153 *et seq.*

few minutes becomes cloudy and iridescent. The precipitation increases with the formation of an amorphous yellow precipitate which runs through the filter. By boiling, it becomes canary-yellow and flocculent, filtering fairly well. The precipitation does not seem to be complete ; it is retarded by the presence of an excess of cobalticyanide or by large quantities of ammonium salts. The precipitate once formed is not soluble in cobalti-cyanide solution, nor in mineral acids, cold or hot, dilute or concentrated. Hydrochloric acid changes the color of the precipi-tate and renders it almost impossible to filter. Insoluble in acetic acid, cold or hot ; when freshly precipitated it is instantly soluble in oxalic acid but reprecipitates on boiling. It seems that at least two different compounds are produced ; they differ both in color and solubility ; the greenish one is soluble in oxalic acid and the yellow one insoluble. The latter is formed by long standing in the cold or rapidly by heating. Both give ferric hydroxide with ammonia or potassium hydroxide in the cold. If the ferric salt and the cobalticyanide solutions are mixed hot, precipitation of the yellow compound is instantaneous, no matter which reagent is in excess. The well-washed ferric cobalti-cyanide gives no red color with ammonium thiocyanate.

Ferrous Cobalticyanide.—Ferrous sulphate and potassium cobalticyanide seem to give a normal ferrous cobalticyanide,—a slightly yellow, amorphous, slow-settling precipitate. When an excess of cobalticyanide is present there is no oxidation or change of color in the ferrous cobalticyanide, even upon long boiling. The precipitation is complete and filters well. With nitric acid, cold and hot, and with hydrochloric and sulphuric acids, hot, there is oxidation. The precipitate darkens in varying degrees, most with nitric and least with sulphuric acid. After treatment with these acids the precipitate filters badly. No change is noticed with acetic or oxalic acids; in the presence of the latter it filters very well. With ammonia the precipitate is partially decomposed in the cold, becoming bluish, and by boiling is com-pletely converted into ferrous hydroxide. With potassium hydroxide it gives a greenish tint, darkening on standing, becoming slate-colored by boiling, forming probably a mixture of ferrous and ferroso-ferric hydroxides.

Manganese Cobalticyanide.—This precipitate, apparently normal, is pure white and filters well. It is insoluble in all cold acids but not absolutely so in hot mineral acids. Alkalies decompose it giving first $Mn(OH)_2$ and later by oxidation, $Mn_2O_2(OH)_2$.

Zinc Cobalticyanide is formed when a solution of zinc sulphate is precipitated by potassium cobalticyanide. It is pure white, settles quickly and filters well ; insoluble in hot water, cold or hot acids, except that a trace seems to dissolve in hot sulphuric acid. This precipitate as well as a few others, *e. g.*, ferrous and ferric cobalticyanides, on boiling with hydrochloric acid passes into a condition which renders it impossible to filter even on double filters. It is very soluble in alkalies.

Cobalt Cobalticyanide.—From solutions of cobaltous chloride, potassium cobalticyanide precipitates a rose-pink, amorphous, rather gelatinous precipitate which is insoluble in cold and hot acids. At 100° or even lower it looses water and becomes blue. This fact was noted by Zwenger, who also states that he formed this compound by heating cobalticyanhydric acid with concentrated sulphuric acid and diluting with water before the decomposition was complete. A peculiarity of many cobalticyanides is the large amount of water which they retain after drying at 100° C. Zwenger noticed that the blue anhydrous cobaltous-cobalticyanide rapidly absorbs moisture from the air and that when water is poured upon it, there is a considerable evolution of heat. We found that the ferrocyanides of zinc and manganese acted in the same way. When cobaltous-cobalticyanide is treated cold with ammonia, it gives a brown solution and pink residue ; on boiling, the solution becomes pink and the residue greenish-brown. The presence of ammonium salts increases the solubility of this compound in ammonia ; it is completely soluble in concentrated ammonia. Caustic potash gives first blue basic salts and on standing or boiling rose-colored cobaltous hydroxide.

Nickel Cobalticyanide results when potassium cobalticyanide is added to solutions of nickel salts. Zwenger states that this precipitate cannot be washed free from potassium salts and that the pure nickel cobalticyanide, $Ni_3Co_2(CN)_{12}$, must be made from cobalticyanhydric acid and a nickel salt. The precipitate is

SOLUBILITIES OF THE COBALTICYANIDES.

$K_3Co(CN)_6$.	(1) HNO₃.	(2) HCl.	(3) H₂SO₄.	(4) H.C₂H₂O₂.	(5) H₂C₂O₄.	(6) NH₄OH.	(7) KOH.	Remarks.
+AgNO₃ white, curdy ppt.	(cold) i (hot) i	AgCl AgCl	i i	i i	i i	partly s s	Ag₂O Ag₂O	Precipitation complete. Settles and filters well. (6) White crystalline ppt. (double salt) on evaporation. Easily sol. cold conc. NH₄(OH).
+Hg₂(NO₃)₂ white, flocculent ppt.	i i	Hg₂Cl₂ Hg₂Cl₂	i i	i i	i i	NH₂Hg₂NO₃ NH₂Hg₂NO₃	Hg₂O Hg₂O	(3) Seems slightly soluble hot or else is partly changed to Hg₂SO₄. (5) Not changed to oxalate.
+CuSO₄, turquoise-blue ppt.	i i	i i	i i	i i	i i	s s	CuO CuO	Filters well. (6) Intense blue solution, giving double NH₃ compound on evaporation. (7) Turns green, getting darker until black CuO separates.
+Bi(NO₃)₃ dense, white ppt.	i i	eas'y s s	i i	i i	i i	i i	Bi(OH)₃ Bi₂O₃	Precipitation done in strongly acid solution to prevent basic salts upon dilution. (6) Not transposed to Bi(OH)₃.
+CdCl₂ white, amorphous ppt.	i i	i s	i i	i i	i i	s s	Cd(OH)₂ Cd(OH)₂	Filters badly. (2) Precipitates again on cooling.
+Fe₂Cl₆ green, becoming yellow.	i i	i i	i i	i i	i i	Fe₂(OH)₆ Fe₂(OH)₆	Fe₂(OH)₆ Fe₂(OH)₆	(5) When freshly precipitated and greenish it is readily sol. in oxalic cold. Ammonia salts in quantity prevent precipitation and excess of K₃Co(CN)₆ retards it.
+FeSO₄ faintly yellowish white ppt.	i i	i i	i i	i i	i i	partly Fe(OH)₂ Fe(OH)₂	Fe(OH)₂ Fe(OH)₂	(1, 2 and 3) On boiling oxidize more or less to yellow ferric cobalticyanide. (6 and 7) Some oxidation to dark-colored ferroso-ferric compounds.
+MnCl₂ white ppt.	i i	i i	i i	i i	i i	Mn(OH)₂ and Mn₂O₃(OH)₂	Mn(OH)₂ and Mn₂O₃(OH)₂	(1, 2, 3, 4, and 5) Seem very slightly soluble hot.
ZnSO₄ dense, white ppt.	i i	i i	trace s	i i	i i	easily s s	easily s s	(4 and 5) Bump violently on boiling.
+CoCl₂ rose-pink ppt.	i i	i i	i i	i i	i i	partly s partly s	Co(OH)₂ Co(OH)₂	(6) Solubility increased by ammonium salts. Almost completely sol. in hot conc. NH₄OH. (7) At first blue basic salts, turning again pink.
+NiCl₂ robin's egg blue ppt.	i i	i i	i i	i i	i i	blue sol. s s	Ni(OH)₂ Ni(OH)₂	Very voluminous precipitate, which filters poorly.
NH₄, Li, Na, Mg, Ba, Ca, Sr, Pb, Hg'', Sn''+IV, Cr, Al, Pt, Au, Zr, Ti, Mo salts.	No precipitates.							Solutions of salts of other metals are not precipitated by K₃Co(CN)₆ and other known cobalticyanides are easily soluble in water. Such cobalticyanides are usually made from an oxide or hydroxide acted upon by H₃Co(CN)₆.

robin's egg blue in color, very voluminous and dries up to a vitreous mass with conchoidal fracture. It is insoluble in water and acids, cold or hot ; soluble completely in ammonia, cold or hot. Potassium hydroxide gives instantly pale green nickel hydroxide.

The effect of the reagents used on the precipitates formed by potassium cobalticyanide is shown by the accompanying table. A glance at this tabulation will show several possibilities for new separations :

1. The lead salt is exceedingly soluble, while those of silver, copper, and bismuth are insoluble in either water or nitric acid. This may find an application in the analysis of pig lead, when the separation of relatively small quantities of these impurities would be much more preferable to the separation of the lead as sulphate. The separation of the bismuth can be effected either by treatment with hydrochloric acid which dissolves the bismuth cobalticyanide and leaves the copper as cobalticyanide and the silver as chloride, or by ammonia which leaves the bismuth and dissolves the copper and silver. The bismuth compound, if not suitable for weighing, can be decomposed by potassium hydroxide and weighed as Bi_2O_3 or one of the new volumetric methods may be employed for its estimation.

2. As the precipitation of ferric cobalticyanide in the cold can be completely prevented by the presence of ammonium sulphate, and probably by other compounds, it is possible to precipitate zinc, manganese, nickel, or cobalt in the presence of iron. With zinc ores containing iron and manganese, the manganese and zinc can be precipitated as cobalticyanides and then separated by treatment with potassium hydroxide, which readily dissolves the zinc cobalticyanide and leaves the manganese as $Mn_2O_3(OH)_2$.

Another possible application is in the analysis of nickel steel, where the separation from ferric iron, if sufficiently complete, would be more convenient than the method in use, based on the solubility of ferric chloride in ether. The nickel cobalticyanide after filtration can be converted into hydroxide and then dissolved in acid for the cyanide titration or for electrolysis.

These and other possible uses of the cobalticyanides are under investigation at Columbia University.

SEVENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED IN 1899.

BY F. W. CLARKE.

T HE year 1899 has not been remarkably prolific in determinations of atomic weight ; and comparatively few investigations have been published. The data are given in the following pages, plus an account of two memoirs which appeared in 1898, but which reached this country only after the report for that year had been printed. These memoirs, by Vandenberghe on molybdenum, and by Kölle on cerium, were issued outside of the usual channels for chemical publication, and so seem to have escaped general notice hitherto.

BORON.

An elaborate memoir upon the atomic weight of boron has been published by Gautier,[1] who worked upon four different compounds. All weights were reduced to a vacuum, and all calculations were made with the atomic weights recommended a year ago by the committee of the German Chemical Society.

First, sulphide of boron was decomposed by a dilute solution of caustic soda ; the solution produced was then oxidized by means of bromine water, and the sulphur was precipitated and weighed as barium sulphate. The results obtained were as follows :

Weight B_2S_3.	Weight $BaSO_4$.	Atomic weight.
0.2754	1.6312	11.032
0.3380	2.0004	11.081
0.3088	1.8300	11.000
0.2637	1.5614	11.050

Mean, 11.041

The second compound studied was the carbide, B_6C. This was heated in chlorine gas to eliminate boron ; the residual carbon was then weighed directly, and afterwards burned in oxygen to reweigh as CO_2. The atomic weights given below were calculated from the weight of the carbon dioxide.

Weight B_6C.	Weight C.	Weight CO_2.	Atomic weight.
0.2686	0.0429	0.1515	11.001
0.3268	0.0512	0.1844	10.994

Mean, 10.997

[1] *Ann. chim. phys.* (7), **18**, 352, November, 1899.

With the third compound, boron tribromide, two series of experiments were made, representing two preparations. The bromide was in each analysis decomposed by water, special precautions being taken to avoid explosive reactions; and the bromine was finally precipitated and weighed as silver bromide. The data are subjoined :

FIRST SERIES.

Weight BBr$_3$.	Weight AgBr.	Atomic weight.
3.1130	6.994	11.009
3.3334	7.490 ♦	10.981
3.7456	8.414	11.043
3.2780	7.364	11.032
4.2074	9.452	11.026

Mean;   11.018

SECOND SERIES.

Weight BBr$_3$.	Weight AgBr.	Atomic weight.
3.3956	7.628	11.037
4.0295	9.052	11.032
3.7886	8.512	11.003
3.1711	7.124	11.026

Mean,   11.025

With boron trichloride the analyses were conducted precisely as in the case of the bromide, silver chloride being the final product weighed.

Weight BCl$_3$.	Weight AgCl.	Atomic weight.
2.6412	9.682	10.987
2.7920	10.234	11.000
2.4634	9.026	11.043
3.4489	12.640	11.013
2.2015	8.070	10.992
2.6957	9.878	11.030

Mean,   11.011

The mean of the values obtained from the bromide and chloride series, 11.016, is the value which Gautier proposes to adopt.

NITROGEN.

Dean[1] has continued the investigation which was reported in 1898, relative to the atomic weight of nitrogen. The ratio studied is that between potassium bromide and silver cyanide, and the value finally found is N = 14.031. Only an abstract of the paper has yet appeared.

[1] *Chem. News*, 80, 279.

CALCIUM.

A paper upon the atomic weight of calcium, by T. W. Richards, was read at the meeting of the American Association for the Advancement of Science in August, but has not, at the date of this report, been fully published. Five analyses of carefully purified calcium chloride were made to determine the ratio $CaCl_2 : 2AgCl$. Calculated with $O = 16$ and $Cl = 35.455$, the values found for Ca range from 40.121 to 40.130, the mean of all being 40.126.

NICKEL.

The work of Richards and Cushman upon the atomic weight of nickel, noticed in the report of 1897, has been continued.[1] The sublimed bromide was reduced in hydrogen, giving the ratio between bromine and the metal. The weights corrected for known impurities, and the values found, are as follows:

Weight NiBr₂.	Weight Ni.	Atomic weight.
2.83325	0.76081	58.705
3.21625	0.86358	58.696
2.31241	0.62094	58.703
2.87953	0.77330	58.710
2.29650	0.61679	58.719
2.98893	0.80272	58.714
5.51291	1.48056	58.716
2.24969	0.60415	58.710
	Mean,	58.709

All weights represent reductions to vacuum, and the antecedent values used in calculation are $O = 16$, and $Br = 79.955$. The complete agreement with the former determinations is almost startling. A full discussion of earlier determinations is given at the close of the paper, and it is shown that the work of Winkler and of Zimmermann is in accord with the new data.

COBALT.

Just as in the case of nickel, Richards and Baxter have extended their observations upon cobalt,[2] and now give three series of new determinations dependent upon the reduction of bromide to metal. In the first series, which is preliminary, a slight impurity is stated as "residue;" in the other series corrected weights are

[1] *Proc. Amer. Acad.*, 34, 327, February, 1899.
[2] *Ibid.*, 34, 351, February, 1899.

given. The nature of the impurity, however, is fully discussed in the paper.

FIRST SERIES.

Weight CoBr₂.	Weight Co.	Residue.	Atomic weight.
5.59216	1.50873	0.00193	59.007
4.61944	1.24807	0.00426	58.996
3.75291	1.01713	0.00793	58.989
3.00645	0.81409	0.00510	59.007
		Mean,	59.000

SECOND SERIES.

Weight CoBr₂.	Weight Co.	Atomic weight.
5.32194	1.43428	58.996
7.50786	2.02321	58.989
2.32630	0.62677	58.973
7.44694	2.00736	59.011
	Mean,	58.992

THIRD SERIES.

Weight CoBr₂.	Weight Co.	Atomic weight.
5.10891	1.37721	59.016
6.41339	1.72850	58.999
6.59805	1.77876	59.021
3.02854	0.81606	58.982
	Mean,	59.004

The mean of the second and third series is 58.998, when $O = 16$ and $Br = 79.955$. Vacuum weights are given throughout.

In a still later paper[1] Richards and Baxter check their determinations of the atomic weight of cobalt by experiments upon the chloride and oxide. The chloride was reduced in hydrogen to metal, and the data obtained, after corrections for known impurities and reduction to a vacuum, were as follows:

Weight CoCl₂.	Weight Co.	Atomic weight Co.
4.16483	1.89243	59.053
2.30512	1.04723	59.035
	Mean,	59.044

The reduction of cobalt monoxide in hydrogen was similarly effected, but with varying results depending upon differences in the conditions cf the experiments.

First, three determinations, with vacuum weights, gave as follows:

[1] *Proc. Amer. Acad.*, 35, 61, August, 1899.

Weight CoO.	Weight Co.	Atomic weight Co.
7.04053	5.53779	58.962
6.69104	5.26312	58.974
7.83211	6.15963	58.927
	Mean,	58.954

These data, which are not sufficiently concordant among themselves or with the bromide determinations, probably indicate that the cobalt oxide contained some excess of oxygen. In a fourth experiment precautions were taken to avoid this difficulty, and 7.74242 grams of oxide gave 6.09219 of cobalt, whence Co = 59.068. In a fifth experiment, resembling the fourth, but with differences in detail, 10.58678 grams of CoO gave 8.32611 of metal, corresponding to an atomic weight of Co = 58.929.

The authors give elaborate particulars as to the circumstances under which each determination was made, and conclude that cobalt monoxide varies too widely in its composition to be suitable for exact measurements of atomic weight. The true value for cobalt undoubtedly lies between 58.93 and 59.07, the figure 58.995, obtained from the bromide, being the most probable.

MOLYBDENUM.

In 1897 the Belgian Academy of Sciences awarded a special Stas prize to M. Ad. Vandenberghe for his determination of the atomic weight of molybdenum. The memoir has recently been published,[1] and the data are now available.

Vandenberghe starts out with molybdenum dibromide, scrupulously purified. From this he obtains metallic molybdenum, by careful reduction in hydrogen at a white heat. The atomic weight determinations are made by the oxidation of Mo to MoO_3, by means of pure nitric acid. The product was finally dried at a temperature of from 350° to 400°, and cooled in a current of oxygen. The data obtained are as follows:

Weight Mo.	Weight MoO_3.	Atomic weight.
0.7143	1.0711	95.851
0.3453	0.5177	95.899
0.9693	1.4533	95.889
0.5089	0.7631	95.854
1.7219	2.5820	95.855
4.2597	6.3872	95.869

[1] *Acad. Roy. des Sciences*, Mémoires Couronnés, 4to. series, Tome 56, 1898.

Reducing all weights to a vacuum, the final value becomes 95.829, when $O = 15.96$. If $O = 16$, $Mo = 96.069$. If $O = 15.88$, then $Mo = 95.349$. This value is very near that found by Smith and Maas, by an entirely different method, but rather higher than that given by Seubert and Pollard. For all practical purposes the value $Mo = 96$ may be assumed.

TUNGSTEN.

Two investigations relative to the atomic weight of tungsten have been published from the laboratory of the University of Pennsylvania. The first one by G. E. Thomas[1] contains a record of experiments upon WO_3 and $Na_2WO_4.2H_2O$. The reduction of oxide to metal, and the reverse process of oxidation, gave figures ranging from 183.51 to 184.22 for the atomic weight of tungsten, and work along this line was discontinued. With sodium tungstate three series of dehydration experiments were made, giving the ratio between water and the anhydrous salt as the measure from which to calculate. These results also were discordant, and Thomas discards the method as unsuited to accurate determinations. The object of the paper seems to be negative, and to show that neither method employed is adequate to its purpose.

The second paper, by Professor Smith, contains a section by W. L. Hardin,[2] of similar purport to that of Thomas. Experiments were made upon the oxide, the oxychloride, barium metatungstate, and the precipitation of silver by metallic tungsten, and each method was found to be defective. Discordant results were obtained in each set of trials. The mean of all experiments upon the reduction of WO_3, and the oxidation of tungsten give approximately the value $W = 184$. This value Hardin thinks it best to accept until more conclusive determinations shall have been made.

CERIUM.

Kölle's dissertation[3] upon this element deals partly with its atomic weight and partly with other matters. His material was obtained from cerite, and was purified with extreme care. Iodo-

[1] This Journal, 21, 373, April, 1899.
[2] Ibid., 21, 1017, November, 1899.
[3] Beiträge zür Kenntniss des Cers. Doctoral Dissertation by Gotthold Kölle, Zurich, 1898.

metric determinations of cerium salts gave, invariably, results which were too high, and which led him to believe that the source of error was in the accepted atomic weight of cerium, an essential factor in his calculations.

Accordingly, new determinations of atomic weight were made by the standard method ; namely, the ignition of cerium sulphate to cerium dioxide. Cerium chloride prepared from the oxide, was spectroscopically examined, and found to be free from other metals. The atomic weight data are as follows, computed with $O \doteq 16$.

Weight $Ce_2(SO_4)_3$.	Weight CeO_2.	Per cent. CeO_2.	Atomic weight.
1.84760	1.11648	60.429	139.11
1.16074	0.70078	60.331	138.78
1.53599	0.92722	60.366	138.73
0.97196	0.58661	60.353	138.64
1.40374	0.84760	60.384	138.84
1.75492	1.05956	60.377	138.80
1.53784	0.92853	60.379	138.82
1.64233	0.99150	60.372	138.76

Mean, 138.81

This value is lower than any of the later determinations, but agrees nearly with that of Wolf. Like Wolf, and like some other recent investigators, Kölle obtained a white ceric oxide, and he regards the colored preparations of former researches as evidently impure. Furthermore, iodometric estimations made on known quantities of ceric oxide gave good results when the new atomic weight was used in calculation, but excesses of 0.8 per cent. when Brauner's or Robinson's value was employed. So far as present evidence goes there is a presumption in favor of Kölle's determination.

PALLADIUM.

Hardin's research[1] upon the atomic weight of palladium is based upon the reduction of certain compounds in hydrogen. Neither of the salts studied had been previously applied to determinations of this character, and the results obtained are therefore of special value. They are, moreover, very concordant, and seem to be more nearly conclusive than any determinations previously made. All weights were reduced to a vacuum, and the

[1] This Journal, 21, 943, November, 1899.

calculations are based upon atomic weights given in the table of your committee for 1898.

First, diphenyl-pallad-diammonium chloride was studied. After reduction, the metal was heated in air to burn off possible free carbon, then reheated in hydrogen, and cooled in air to prevent occlusion of the former gas.

Weight of salt.	Weight Pd.	Atomic weight.
0.98480	0.28953	107.06
1.10000	0.32310	106.92
1.02820	0.30210	106.96
1.19230	0.35040	107.00
1.40550	0.41300	106.98
1.26000	0.37040	107.04
2.25510	0.66310	107.08
	Mean,	107.006

The second series of determinations was made upon diphenyl-pallad-diammonium bromide, with the following results :

Weight of salt.	Weight Pd.	Atomic weight.
0.88567	0.20917	107.01
1.31280	0.31000	106.99
1.50465	0.35540	107.03
2.01635	0.47635	107.05
2.92300	0.69080	107.10
	Mean,	107.036

Finally, ammonium palladium bromide was studied, giving four more determinations.

Weight of salt.	Weight Pd.	Atomic weight.
0.77886	0.18006	107.03
1.53109	0.35381	106.96
2.75168	0.63614	107.03
1.88136	0.43478	106.98
	Mean,	107.00

The mean of all three series, when O = 16, is 107.014. 107 then, may be taken as the most probable value for the atomic weight of palladium.

RADIUM.

Madame Curie,[1] having prepared a large quantity of radiferous barium chloride, has determined the chlorine in several fractions

[1] *Chem. News*, 80, 793.

of the material, and so ascertained the atomic weight of the metal contained in it. Three determinations gave for this atomic weight:

<div style="text-align:center">

140.0

140.9

145.8

</div>

Hence the atomic weight of radium is higher than that of barium, although its true value is still unknown.

THE ELECTROCHEMICAL EQUIVALENTS OF COPPER AND SILVER.

This subject has been reinvestigated somewhat elaborately by Richards, Collins, and Heimrod.[1] First, copper was precipitated in comparison of the silver and copper voltameters, under varying conditions as to temperature, character of solution, and size of plates, and the results are summarized as follows for the atomic weight of copper, when $Ag = 107.93$.

Large plates, cupric solutions, t. 20°,				$Cu = 63.47$
" " " " t. 0°,				63.525
Small " " " t. 0°,				63.547
Medium " cuprous " t. 0°,				63.573
" " " " t. 60°,				63.615
Corrected results from cupric solutions,				$Cu = 63.563$

a value 0.041 lower than that determined by chemical processes.

A study of the silver voltameter by itself showed that it gives results which are too high by about 0.081 per cent. Correcting the atomic weight of copper in accordance with this observation, the true value is found to lie between 63.598 and 63.615. The value previously established by Richards was 63.604, a confirmation of the present work, which is to be continued.

TABLE OF ATOMIC WEIGHTS.

In the following table of atomic weights your committee give first its own set of values, based upon both fundamental standards. Next is given Richards' table, revised for 1899, and finally that of the German Chemical Society. The values in the German table are rounded off to convenient approximations for practical use; those of Richards give the nearest significant figure, and the latter policy, which is wise, has also been adopted by your committee. There are, however, slight differences of

[1] *Proc. Amer. Acad.*, 35, 123, December, 1899.

opinion in some cases as to where the nearest significant decimal place really is.   Hardin's work on palladium and tungsten, and Kölle's research on cerium, have led to the only notable changes from last year.

| | Clarke. | | | |
	H = 1.	O = 16.	Richards.	German.
Aluminum	26.9	27.1	27.1	27.1
Antimony	119.5	120.4	120.0	120.
Argon	?	?	39.9?	40.
Arsenic	74.45	75.0	75.0	75.
Barium	136.4	137.40	137.43	137.4
Bismuth	206.5	208.1	208.0	208.5
Boron	10.9	11.0	10.95	11.
Bromine	79.34	79.95	79.955	79.96
Cadmium	111.55	112.4	112.3	112.
Caesium	131.9	132.9	132.9	133.
Calcium	39.8	40.1	40.1	40.
Carbon	11.9	12.0	12.001	12.00
Cerium	138.0	139.0	140.	140.
Chlorine	35.18	35.45	35.455	35.45
Chromium	51.7	52.1	52.14	52.1
Cobalt	58.55	59.00	59.00	59.
Columbium	93.0	93.7	94.	94.
Copper	63.1	63.6	63.60	63.6
Erbium	164.7	166.0	166.	166.
Fluorine	18.9	19.05	19.05	19.
Gadolinium	155.8	157.0	156. ?	....
Gallium	69.5	70.0	70.0	70.
Germanium	71.9	72.5	72.5	72.
Glucinum	9.0	9.1	9.1	9.1
Gold	195.7	197.2	197.3	197.2
Helium	?	?	4.0?	4.
Hydrogen	1.000	1.008	1.0075	1.01
Indium	113.1	114.0	114.	114.
Iodine	125.89	126.85	126.85	126.85
Iridium	191.7	193.1	193.0	193.
Iron	55.6	56.0	56.0	56.
Lanthanum	137.6	138.6	138.5	138.
Lead	205.36	206.92	206.92	206.9
Lithium	6.97	7.03	7.03	7.03
Magnesium	24.1	24.3	24.36	24.36
Manganese	54.6	55.0	55.02	55.
Mercury	198.50	200.0	200.0	200.3
Molybdenum	95.3	96.0	96.0	96.
Neodymium	142.5	143.6	143.6	144.
Nickel	58.25	58.70	58.70	58.7

| | Clarke. | | | |
	H = 1.	O = 16.	Richards.	German.
Nitrogen	13.93	14.04	14.045	14.04
Osmium	189.6	191.0	190.8	191.
Oxygen	15.88	16.000	16.0000	16.00
Palladium	106.2	107.0	106.5	106.
Phosphorus	30.75	31.0	31.0	31.
Platinum	193.4	194.9	195.2	194.8
Potassium	38.82	39.11	39.140	39.15
Praseodymium	139.4	140.5	140.5	140.
Rhodium	102.2	103.0	103.0	103.
Rubidium	84.75	85.4	85.44	85.4
Ruthenium	100.9	101.7	101.7	101.7
Samarium	149.2	150.3	150.0	150.
Scandium	43.8	44.1	44.	44.1
Selenium	78.6	79.2	79.2	79.1
Silicon	28.2	28.4	28.4	28.4
Silver	107.11	107.92	107.930	107.93
Sodium	22.88	23.05	23.050	23.05
Strontium	86.95	87.60	87.68	87.6
Sulphur	31.83	32.07	32.065	32.06
Tantalum	181.5	182.8	183.	183.
Tellurium	126.5	127.5?	127.5?	127.
Terbium	158.8	160.	160.	....
Thallium	202.61	204.15	204.15	204.1
Thorium	230.8	232.6	233.	232.
Thulium	169.4	170.7	170.?	....
Tin	118.1	119.0	119.0	118.5
Titanium	47.8	48.15	48.17	48.1
Tungsten	182.6	184.	184.4	184.
Uranium	237.8	239.6	240.	239.5
Vanadium	51.0	51.4	51.4	51.2
Ytterbium	171.9	173.2	173.	173.
Yttrium	88.3	89.0	89.0	89.
Zinc	64.9	65.4	65.40	65.4
Zirconium	89.7	90.4	90.5	90.6

PRELIMINARY COMMUNICATION ON THE CHEMISTRY OF MUCIN.[1]

BY P. A. LEVENE.

THE proteids may be divided into two main groups : First, simple proteids, second, combined proteids. Of the latter the most common are the nucleo-compounds and the mu-

[1] Read before the New York Section of the American Chemical Society, November 10, 1899.

cins. The mucins at present are considered to be compounds of
proteids with carbohydrates. This assumption is based on the
fact that all the mucins and allied compounds yield, on prolonged
treatment with dilute mineral acids, substances reducing Fehling's
solution in the same manner as glucose. The true nature of
these substances was, however, unknown to the first workers on
mucin.

The first successful attempt to obtain a pure carbohydrate was
made in Hoppe-Seyler's laboratory. Landwehr stated that he ob-
tained from various mucins a substance very similar in its proper-
ties to gum and named it "animal gum." He did not, however,
view mucin as consisting of proteid and animal gum, molecularly
combined. In his opinion mucins were only a mixture of the
two substances. His views on this latter point were subsequently
retracted by the author. After Landwehr almost every investi-
gator working on this subject sought for the same "animal gum,"
and many claimed to have obtained it. Hammarsten succeeded
but once in obtaining from mucin a nitrogen-free substance,
which, on heating with mineral acids, was capable of reducing an
alkaline copper solution. Loebish asserted that by following the
conditions indicated by Landwehr he obtained the same "animal
gum" from the mucin of fibrous tissue.

A new series of investigations on the entire question of "ani-
mal gum" was very recently undertaken by Folin in Hammar-
sten's laboratory. The latter doubting for certain reasons the
correctness of Landwehr's statements, followed as closely as pos-
sible all the conditions prescribed by Landwehr, the substances
thus obtained never being free from proteid material. Instead
of "animal gum" he obtained a "mucinalbumose." Most of
the other workers investigated only the composition of the various
mucins as such, or the "carbohydrates" resulting from heating
the mucins with dilute mineral acids.

There is, however, one property of all the mucins, to which
sufficient attention has not been directed. The mucins possess
very marked acid properties, more distinct than any simple pro-
teid, and, in fact, more than any carbohydrate, which display no
acid character whatever. In explanation of the acid properties
two assumptions may be made : First, the substance reducing
copper (formed on heating with mineral acids), may be an acid

derivative of some carbohydrate, and secondly, there may be
some acid besides the proteid and carbohydrate in the mucin
molecule.   Loebisch had already noticed that his "animal gum"
would decompose carbohydrates, and Hammarsten stated that
he could obtain a substance with acid properties from mucins.

The object of this work was to make a thorough study of the
acid part of the mucin molecule.   My first experiments were
made on tendo-mucin obtained according to the method of Chit-
tenden and Gies.   The pure mucin was treated for twenty-four
to forty-eight hours with a 2 per cent. sodium hydroxide solu-
tion and from this solution a substance with acid properties was
obtained, by a very simple method, which will be described
when the work is completed.

On more detailed examination the substance proved to be ni-
trogenous. It did not, however, give the biuret reaction, and con-
sequently was free from proteids.   On boiling with dilute hydro-
chloric acid the substance reduced Fehling's solution.   The solu-
tion of the substance on addition of hydrochloric acid and barium
chloride remained perfectly clear, but on boiling yielded a white
precipitate.   All these properties are peculiar to chrondroitin-
sulphuric acid.   Hence it was natural to assume some relation-
ship between the two substances.   Two grams of the substance
were heated on a water-bath in 100 cc. of 3 per cent. nitric acid
until the solution gave no precipitate with alcohol (this con-
sumed about twenty hours).   Several volumes of alcohol and
ether were then added to this solution.   This yielded only an
opalescence ; upon addition of a few drops of sodium chloride so-
lution, however, a fine white precipitate formed, which gave the
barium test for chrondrosin.

The substance gave a precipitate with a solution of Witte's
peptone only on addition of acetic acid as long as there was still
some of the sodium salt present.   When the acid was free from
sodium salts, it gave on standing with a neutral albumose solu-
tion a flocculent slimy precipitate, resembling genuine mucin.
Copper, sodium, and barium salts of the substance were also
obtained.

ANALYSIS OF THE COPPER SALT.

0.358 gram of the substance was decomposed with hydrochloric
acid ; the copper was precipitated with hydrogen sulphide and

weighed as CuO ; o.o446 gram CuO, or 9.97 per cent. metallic copper was obtained.

Schmiedeberg found the percentage of copper varying between 9.04 and 10.20 per cent. In all these properties, as well as the copper content, this substance resembles chrondroitinsulphuric acid.

The next question was whether this ethereal or compound sulphuric acid was only a contamination of the mucin, or constituted an integral part of it. Some of the mucin prepared as above was dissolved in 1 per cent. sodium carbonate, and immediately treated as before for the isolation of the acid ; only traces were, however, obtained. The residue was washed and redissolved and again treated in like manner ; here also only traces were detected. The residue was then thoroughly washed with distilled water until the substance was entirely washed out. The residue was left for twenty-four hours in 200 cc. of 2 per cent. solution of sodium hydroxide. It was then treated as above for the isolation of the substance. The yield was a very good one. I also observed that the acid can be split off from mucin on digesting the latter on the water-bath with addition of a few drops of hydrochloric acid. On digestion with pepsin-hydrochloric acid the mucin also yielded the same acid even after twenty-four hours of digestion. After three weeks of digestion part of the mucin, however, remained undissolved. The investigation into the nature of the residue, as well as of the proteases thus formed, has so far not been completed.

The next question was whether only the tendo-mucin is a compound of an ethereal sulphuric acid, or whether all the mucins and mucoids have the same composition. The investigation before us thus far embraces only the submaxillary mucin and the substance of a mucoid carcinoma. The submaxillary mucin was obtained by the following method: Freshly removed glands were placed in ether immediately after the death of the animal, and then brought to the laboratory. There they were minced in a chopping machine and allowed to macerate with distilled water for twenty-four hours (large quantities of chloroform being added to keep the tissue from decomposing). The extract was then strained through gauze, well shaken with ether in separatory funnels, and left in the latter for twenty-four hours.

This process caused all the tissue particles and the fat to collect on the surface, the lower layer remaining perfectly clear. It was then filtered and treated for mucin according to the method of Hammarsten. The substance was redissolved and reprecipitated twice. This mucin was treated in the same way as the tendo-mucin for the ethereal sulphuric acid. But instead of the latter a substance was obtained very similar to that obtained by Folin in Hammarsten's laboratory, and which he called mucinal-bumose.

After several futile attempts to obtain the acid free from proteids I finally obtained positive results by the following method: The mucin was digested for one hour in a Koch sterilizer with 0.1 per cent. hydrochloric acid solution. The solution, being then neutralized with sodium hydroxide, was treated with large quantities of alcohol. The precipitates thus formed were treated with 5 per cent. sodium hydroxide and allowed to stand over night. This solution was treated in two different ways, each yielding positive results: (1) The solution was treated with Brucke's reagent and hydrochloric ,acid. The filtrate did not give any precipitate on addition of alcohol and ether. If, however, a sufficient quantity of sodium hydroxide was added previously to the alcohol to render the solution slightly alkaline, a yellowish precipitate was formed very similar to that of the sodium salt of the ethereal sulphuric acid. The precipitate was redissolved in dilute sodium hydroxide solution, filtered and reprecipitated with alcohol. The substance thus obtained precipitated an acid solution of albumose, reduced Fehling's solution on boiling with hydrochloric acid, and on addition of hydrochloric acid and barium chloride gave a precipitate only upon heating. It was nitrogenous and did not give the biuret reaction. There was not enough of the substance to attempt the chrondrosin test.

In another experiment phosphotungstic acid was used instead of Brucke's reagent. The result was the same

From this may be· concluded that the submaxillary mucin contains in its molecule a substance which is either chondroitin-sulphuric acid or closely related to it. The investigation of a mucoid carcinoma by the same method as the submaxillary mucin revealed the presence of a similar substance. The study

of ovomucoid, mucoid of the thyroid gland and of a mucoid tumor is now in progress.

I was prompted to make the present communication by the fact that about ten days ago an article appeared in Hoppe-Seyler's *Zeitschrift*. The author analyzed an ovarial mucoid and found a substance similar to chondroitinsulphuric acid. His findings on the latter mucoid coincide with mine on several mucins and justify the conclusions I was ready to draw from my work, that mucins are not simple compounds of proteids and carbohydrates, but are proteid derivatives of an ethereal sulphuric acid.

I consider it premature at this moment to state positively the nature of this combination.

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THE DETERMINATION OF GLYCOGEN AND RELATIVE QUANTITIES OF GLYCOGEN IN DIFFERENT PARTS OF THE FLESH OF A HORSE.

BY J. K. HAYWOOD.

A GREAT many methods have been proposed for the estimation of glycogen,[1] but on trying them I found that nearly all were open to some serious objection, which rendered their employment either entirely out of the question or the results obtained very doubtful. I have, therefore, worked out a method which, although not new in principle, is new in many of the details which go to making up a fairly accurate and speedy procedure. But first I will speak of some of my preliminary experiments to show future workers in this field, at least, what *not to do*.

[1] Wiley's "Principles and Practice of Agricultural Analysis", 3, 554.

Having seen in a paper by Von Wittich[1] that glycogen might be determined by digesting the sample of meat on the steam-bath for two or three hours, with water containing a few drops of sulphuric acid, filtering, neutralizing, filtering again, determining the reducing sugar in the filtrate by Fehling solution, and from that figure calculating the glycogen, I thought I would try this, as it seemed the easiest way. I added, however, more than a few drops of sulphuric acid,—in fact, made a 3 per cent. solution; for it is well known that glycogen is more resistant to the action of acids than starch, and a few drops of sulphuric acid would not convert starch in this time. I also continued the digestion for six hours. I encountered a difficulty at once; i. e., the mixture would not filter after digestion, except very slowly,—so slowly that a practical use of the method was impossible. I therefore neutralized immediately after digestion, made to a volume, and filtered off an aliquot portion, which still took a long enough time, but was much shorter than filtering the whole. Using a dried, ether-extracted liver, I obtained results of 1.27 and 1.29 per cent. glycogen, which looked encouraging from the closeness of the duplicates. The Fehling solution filtrate, however, looked dirty, and the copper suboxide precipitated was not red, but a dirty green, such as no chemist likes to see.

I therefore carried through a sample of the liver, using the above method, except that at the end the solution was clarified with lead subacetate, the excess of lead removed by sodium sulphate, and the dextrose determined in the filtrate. In this way a clear Fehling filtrate was obtained, but the results did not at all compare either with each other or with those (1.29 and 1.27) mentioned above. In one case I obtained a result of 0.87 per cent. glycogen, and in a duplicate 0.00 per cent. glycogen.

Thinking from the work of Külz and Bornträger[2] that hydrochloric acid might be a better agent to convert the glycogen to dextrose, I next boiled some of the liver for three hours with 200 cc. of water and 20 cc. of hydrochloric acid (sp. gr. 1.125), neutralized with sodium carbonate, and filtered just as in the determination of starch. The result on a non-clarified portion was 4.72 per cent. glycogen, and on a portion clarified by lead

[1] Central-Blatt. f. d. med. Wissenschaft, 13, 292 (1875).
[2] Archiv. f. d. ges. Physiologie. 24, 28.

subacetate, and the excess of lead removed by sodium sulphate, the result was 1.25 per cent. glycogen. I again determined the glycogen as above, except that the solution at the end was clarified with neutral lead acetate, and results of only 0.03 and 0.04 per cent. glycogen were obtained.

I next added 1 per cent. of starch to a sample of meat which gave no glycogen by the above method, and 1 per cent. of glycogen to another portion of the same meat. The samples thus prepared were treated just as in the determination of starch, and at the end clarified with neutral lead acetate, and the excess of lead removed. Proceeding in this way I could only recover 0.08 per cent. starch and 0.00 per cent. glycogen.

With results thus varying in the case of a sample of liver from 0.00 per cent. to 4.72 per cent., and results of 0.00 per cent. and 0.08 per cent., where 1 per cent. of glycogen and 1 per cent. of starch respectively had been added, it appeared that the method was absolutely worthless ; so it was abandoned.

It may seem strange, at first sight, that no better results than the above could be obtained following after Külz & Bornträger[1] who had worked out a method based on the inversion of glycogen to dextrose and the determination of the latter by Fehling solution ; but this apparent contradiction will disappear when I call attention to the fact that Külz only worked on *pure* glycogen, and in no case mixed his glycogen with meat and recovered it.

I did not make an attempt to estimate glycogen by means of the polariscope, as also given by Külz,[2] because Külz had worked with rather large quantities, so that if only 0.00 to 1.5 per cent. of glycogen were present the determination would be very uncertain, since if a workable quantity of the meat were used (say 50 to 60 grams), the reading on the sugar scale would be only a few tenths of a degree.

Estimating glycogen by the depth of its color with iodine, according to Goldstein,[3] was not employed, as it has been shown to be worthless by many subsequent investigators.

A qualitative test for glycogen by the test of Bräutigam and

[1] *Archiv. f. d. ges. Physiologie*, **24**, 28.

[2] *Ibid.*, **24**, 87 and **24**, 90.

[3] *Verhandlungen der physik-med. Gesell. in Würzburg*, **7**, 1.

Edelmann,[1] by means of iodine, was not employed, because subsequent investigators have been able to obtain the same test with other meats besides horse meat, notably on beef.

I therefore decided to try the method of Brücke,[2] which appeared to promise better results than any of the other gravimetric methods. Brücke digests the meat on the steam-bath with water, filters, precipitates the proteid matter in hydrochloric acid solution with the double iodide of potassium and mercury, again filters, precipitates the glycogen in the filtrate with alcohol, filters on a weighed filter, washes first with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether, dries at 115° C., and weighs. This method has been examined by many later investigators. Külz[3] found that an extraction of the meat with water was not sufficient, but that it was better to employ a weak solution of potassium hydroxide. Kratschmer[4] found that the hydrochloric acid of the Brücke reagent acted on the freshly precipitated glycogen ; also that it was best to first dry the glycogen at 80°–100° C., and then at 115°. I took all of these points into consideration when working out the method.

But first of all a serious difficulty was met with. It was found impossible to filter the meat digested with potassium hydroxide in a reasonable length of time, and nearly impossible to get off any fair-sized aliquot portion. Instead of filtering after the digestion with a weak solution of potassium hydroxide, the mixture was made immediately acid with hydrochloric acid, in the presence of the unattacked residue, Brücke's reagent added to precipitate proteid matter, the whole made to a volume, and an aliquot portion filtered off. In this way a very easily filterable mass was obtained. After an aliquot portion, say 250 cc. out of 500 cc., had been thus obtained, it was neutralized with a solution of potassium hydroxide (using a drop of phenolphthalein as indicator, and noting the amount of hydroxide employed) to get rid of the hydrochloric acid, which would, according to Kratschmer, act on the glycogen. When exact neutralization had been obtained, small flakes of some non-glycogen material would usually separate out. These were filtered

1 *Ztschr. anal. Chem.*, **33**, 98.
2 *Central-Blatt f. d. med. Wissenschaft*, 1871, 388.
3 *Ztschr. für Biologie*, **22**, 161.
4 *Archiv. f. d. ges. Physiologie*, **24**, 134.

off, a few drops of hydrochloric acid added to the filtrate, and twice the volume of 92 to 95 per cent. alcohol added. The precipitated glycogen was, at the end of a few hours, filtered off through a weighed filter, washed first with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether, dried at 80°-100° C., then at 115° C. and weighed again, the gain representing glycogen. In this way a result of 0.51 per cent. was obtained on a dry roast beef, and where 0.87 per cent. and 1.61 per cent. glycogen were added, 0.82 per cent. and 1.54 per cent. respectively were recovered. In each of the above determinations, however, something seemed to come down besides the glycogen, and on treating the filter with hot water this would mostly remain as a residue, and the glycogen be dissolved. It appeared from this, then, that a much better method than the one above was to weigh the filter and contents after drying, then dissolve out glycogen with water, dry and weigh again, and thus determine glycogen by the difference in weight. To test this I carried through a sample of roast beef, and on the water-free, fat-free sample by first method obtained a result of 0.3 per cent. glycogen ; by second, 0.17 per cent. glycogen ; on a liver I obtained 1.53, 1.56 per cent. by the first, and by second, 1.04, 1.10 per cent.; on a chicken I obtained 0.35 per cent. by the first, and by the second 0.26 per cent. It would therefore appear that all of the proteid matter was not precipitated by the double iodide of potassium and mercury, but that some which was nearly entirely insoluble in water came down with the glycogen and remained on the filter when the glycogen was dissolved.

From all of the above work I have settled upon the following method for determining glycogen. From 50 to 60 grams of meat, after having been run through a sausage grinder, is treated in an evaporating dish with 300 cc. of a 1 per cent. potassium hydroxide solution, and heated on the steam-bath for about six hours, water being added from time to time, so that the volume never becomes less than 150 cc. Finally the water is removed by evaporation until about 150 cc. remain. This is made slightly acid with hydrochloric acid (1–5), and hydrochloric acid and double iodide of potassium and mercury[1] added alternately until all pro-

[1] The double iodide of potassium and mercury is prepared by first precipitating a solution of mercuric chloride with potassium iodide, washing the precipitated mercuric iodide till free of chlorides, then saturating a 10 per cent. potassium iodide solution with the mercuric iodide at the boiling temperature.

teid matter is precipitated. The hydrochloric acid is added about 2 cc. at a time, and the double iodide of potassium and mercury about 10 cc. at a time. Usually about 20-25 cc. acid (1–5) and 70–100 cc. of the iodide solution are required. When the proteid matter separates, and leaves a clear liquid layer above, a small amount of this is carefully poured off and tested for complete precipitation. If the precipitation is not complete the liquid is returned, and the proteid precipitant added until the clear liquid above the proteid matter gives no precipitate with hydrochloric acid and .the double iodide solution. Sometimes, not often, the proteid matter will not separate. In this case follow Külz's method of nearly neutralizing with potassium hydroxide and adding again hydrochloric acid, and the precipitate will usually flocculate. The proteid matter being now precipitated as completely as possible, the whole is transferred to a 500 cc. flask, made to the mark with water, well shaken, and an aliquot portion (say 250 cc.) filtered through a fluted filter. A drop or two of phenol phthalein is now added, and the solution titrated to exact neutrality with a concentrated solution of potassium hydroxide, noting the amount used. If a slight amount of flakey-looking matter separates at this point, the liquid is again passed through a fluted filter, and such a volume taken as will correspond to 2/5 of the original material, of course taking into consideration the number of cubic centimeters of potassium hydroxide used to neutralize the hydrochloric acid. Three or four drops of concentrated hydrochloric acid are now added, and twice the volume of from 93 to 95 per cent. alcohol. After standing two or three hours the precipitated glycogen is filtered off through a paper filter, washed with 60 per cent. alcohol, then with 95 per cent. alcohol, then with ether; dried at 80°–100° C., then at 115° C., and weighed in a weighing tube. The filter is then extracted thoroughly with boiling water, dried again at 115° C., and again weighed in a weighing tube, the difference in weight representing glycogen.

Proceeding in this way, I obtained on roast beef 0.17 per cent. glycogen, calculated to the dry, fat-free basis; where 0.87 per cent. glycogen was added, 0.78 per cent. was recovered; and where 1.72 per cent. glycogen was added, 1.57 per cent. was

recovered. Close duplicates were also obtained by this method, as shown from the following work :

On a liver the results were 1.04 and 1.10 per cent. calculated to dry, fat-free basis.

On a chicken the results were 0.26 and 0.29 per cent. calculated to dry, fat-free basis.

On an ox tongue the results were 0.27 and 0.30 per cent. calculated to dry, fat-free basis.

On another ox tongue the results were 0.65 and 0.62 per cent. calculated to dry, fat-free basis.

Following will be found the analysis of three parts of three different horses, the glycogen of which was determined by the above method. First I will mention, however, that in addition to the direct determination of glycogen I also estimated the reducing sugars in a water extract of each sample of meat, as suggested by Niebel[1] to find the amount of glycogen that had been converted to dextrose. This was done by boiling the meat three separate times with 500 cc. portions of water, pouring off the water each time, evaporating to a small volume, clarifying with neutral lead acetate, removing excess of lead with sodium carbonate, making to a volume, filtering off an aliquot portion, and determining the dextrose in the filtrate by Allihn's method.

No. of sample.	Part of horse.	Water.	Fat.	Glycogen.	Glycogen corresponding to dextrose.	Glycogen in each of the preceding columns calculated to fat-free, water-free basis.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	chuck	70.57	9.01	0.30	0.00	1.47	0.00
2	chuck	74.30	4.63	0.48	0.00	2.28	0.00
3	chuck	77.22	5.84	0.86	0.00	5.08	0.00
4	rib	66.12	12.51	0.61	0.00	2.85	0.00
5	rib	72.87	4.54	0.54	0.00	2.39	0.00
6	rib	76.31	1.24	0.79	0.00	3.52	0.00
7	flank	57.93	25.01	0.42	0.00	2.46	0.00
8	flank	71.79	7.66	0.33	0.00	1.61	0.00
9	flank	76.39	1.16	0.53	0.00	2.36	0.00

In four of the above samples a determination was made of the amount of nitrogen in the glycogen dissolved from the filter, to

[1] *Ztschr. f. Fleisch. u. Milch. Hygiene*, 1, 185, 210, and 5, 86, 130.

see how much, if any, proteid matter had not been removed, but still contaminated the glycogen.   In four more of the above samples a determination was made of the amount of ash in the glycogen to see if a correction was necessary.   The results are given below.

No. of sample.	Amount of original beef used.	Amount of beef used in actual determination, being 2/5 of original.	Amount of glycogen found.	Amount of proteid matter $6.25 \times N$.	Amount of ash.
	Grams.	Grams.	Grams.	Grams.	Grams.
1	60	24	0.0717	0.0009	....
2	60	24	0.1148	....	0.0048
3	60	24	0.2070	....	0.0065
4	60	24	0.1467	0.0018	....
5	60	24	0.1304	0.0017	....
6	60	24	0.1898	0.0024	....
7	60	24	0.0999	....	0.0030
9	60	24	0.1282	....	0.0025

It will thus be seen that only a small percentage of the glycogen consists of proteid matter and ash, and when these two are added together, and calculated back as per cent. of the original substance, the figure for glycogen will only be altered by about 0.02 per cent.

In several other determinations of glycogen, the glycogen which was dissolved from the filter was evaporated to a small volume and tested with Brücke reagent and with bromine, to see if any proteid matter was precipitated.   In no case did any come down.

From this work it will be seen that the glycogen obtained is quite pure, only a small portion consisting of ash and proteid matter.   The small plus error caused by these substances, in all probability, about balances the negative error caused by the action of hydrochloric acid on the glycogen during the precipitation of proteid matter.

While the above method is, I think, much more accurate than the original Brücke method, it does not possess the accuracy of a chlorine or sulphuric acid determination, but this is not necessary, since the end of the work is not to know the amount of glycogen to 0.01 per cent., but to distinguish horse meat from other meats by its high content of glycogen.

Appended will be found analyses of several parts of a single horse. These are not given to show anything about the accuracy of the method, but to increase the data relating to the amount of glycogen in different cuts of horse meat. The horse was one which had been killed in an accident, three days before the analysis was made.

No. of sample.	Part of horse.	Water.	Fat.	Glycogen.	Glycogen corresponding to dextrose.	Glycogen in each of the preceding columns, calculated to fat-free, water-free basis.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Second cut of round··	74.36	3.27	0.49	0.00	2.19	0.00
2	First cut of round····	73.77	3.23	0.27	0.05	1.17	0.22
3	Shoulder clod········	73.54	5.27	0.58	0.05	2.73	0.23
4	Cross ribs···········	73.86	6.30	0.32	0.04	1.62	0.20
5	Chuck···············	68.00	15.39	0.34	0.00	2.05	0.00
6	Plate ··············	52.16	33.66	0.41	0.00	2.89	0.00
7	Brisket ·············	66.70	12.16	0.46	0.006	2.17	0.03

I would like to express my thanks to Dr. W. D. Bigelow, of this Division, for putting at my disposal a very complete bibliography of glycogen. Since his work will shortly appear in print, I will not attempt to go into the literature of the subject.

THE ELECTROLYTIC DEPOSITION OF BRASS.

By J. LIVINGSTON R. MORGAN.

BRASS plating by electrolysis was discovered in 1841, and the original process, with a few modifications, is still in use at the present time. The formulas for the preparation of the bath are entirely empirical, the subject, so far as I know, having never been treated from the theoretical standpoint. The purpose of this paper is to consider the reaction by the light of our present knowledge of electrochemistry, and to present the theory of the process which results.

When a metal with a high electrolytic solution pressure (Zn) is placed in an acid solution and connected by a wire to a plate of platinum, immersed in the same liquid, hydrogen gas is

given off, at the platinum side, in the form of bubbles. The chemical reaction is

$$M + \overset{+}{H} + \overset{-}{A} = \overset{+}{M} + \overset{-}{A} + H \text{ gas},$$
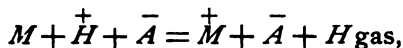
where M represents a monovalent metal, and HA a monobasic acid, which is dissociated into the ions $\overset{+}{H}$ and $\overset{-}{A}$. The process consists, essentially, in, the formation of metallic ions, which force ions of hydrogen out of the solution. A certain difference of potential results from this reaction which may be calculated by aid of the formula

$$\pi = \frac{0.0002}{n} \ T \log. \frac{P}{p} - 0.0002 \ T \log. \frac{P_1}{p_1} \text{ volts},$$

where n is the valence of the metal, P its electrolytic solution pressure, and p the osmotic counter pressure of the metallic ions in solution, while P, and p, are the corresponding figures for hydrogen. The end of such a reaction will be reached, of course, when the solution is saturated with ions of the metal; *i. e.*, when all ions of hydrogen have disappeared.

When a metal possessing a low electrolytic solution pressure (Cu) is placed in acid, no hydrogen gas is given off, and ions of this metal in a solution would precipitate in the metallic form upon the plate.

When the metal plate in the above arrangement is used as the anode of a decomposition cell the general action of a metal with a high electrolytic solution pressure is the same, only intensified. With a metal of low electrolytic solution pressure the action is reversed so that if the electromotive force is made sufficiently high the metal acts as one of the former class and separates hydrogen from the acid. The value of the term P then can always be increased by an external electromotive force. Thus by reversing a Daniell cell and sending a current from the copper to the zinc, through the liquid, copper is dissolved and zinc precipitated. If a solution of a copper salt is electrolyzed with a copper anode, the value of P is increased until it exceeds the value p; *i. e.*, the osmotic counter pressure of the copper ions. At the cathode the copper ions accumulate, and are forced out of a solution upon the plate. With copper this would naturally take

place even without a great accumulation of ions, but with a metal of high electrolytic solution pressure the ions would separate only when the term p is made greater than P. The work necessary for plating with a metal of high electrolytic solution pressure is thus seen to be done at the cathode, for there P must be exceeded by p, while for one with a low electrolytic solution pressure it is done at the anode for there it is necessary for P to exceed p in value.   In other words metals like zinc, in simple solutions, need the current to separate them from the solution, while those like copper need it to cause the anode to dissolve.   If the decomposing electromotive force is great enough, hydrogen will also be separated at the cathode, for ions of hydrogen will accumulate then and be evolved as gas when the electromotive force causes p_1 to exceed P_1 in value.   With a small electromotive force, however, this will not take place so that for our purposes we may leave it out of consideration entirely.

If an alloy, made up of two metals one of which has a very high electrolytic solution pressure, while the other has a very low one, is placed in acid the constituent with the high pressure will dissolve, separating hydrogen gas upon a platinum plate, while the other will be unaffected.   The end of the reaction will be reached when the acid is saturated with the ions of the one metal or if there is an excess of acid, when the one metal is entirely dissolved.   Using such an alloy as the anode of a decomposition cell, both constituents will go into solution.   The amounts dissolved will be proportional to the values of the electrolytic solution pressure.   If the electrolyte in the cell contains ions of each constituent, then at any one decomposing electromotive force the amounts dissolved will be proportional to the electrolytic solution pressures divided by the osmotic counter pressures of the metallic ions.   If the alloy contains 50 per cent. of each constituent it will be necessary for its solution in unchanged ratio, that $\dfrac{P}{p} = \dfrac{P'}{p'}$, where P and P' are the electrolytic solution pressures of the two metals and p and p' the osmotic pressures of their ions.   In other words it is necessary that the ionic concentration of the metals be proportional to the electrolytic solution pressures. This relation is shown most plainly by the following diagram :

$$\left.\begin{array}{l}\text{Cu} \\ \text{Zn}\end{array}\right\} 50 \text{ per cent.} \quad \left[\begin{array}{l} \rightarrow P_{Cu} = 4.8 \times 10^{-20}\text{At.} \\ \rightarrow p_{Cu} = 4.8 \times 10^{-20}\text{At.} \\ \leftarrow p_{Zn} = 9.9 \times 10^{+18}\text{At.} \\ \rightarrow P_{Zn} = 9.9 \times 10^{+18}\text{At.}\end{array}\right.$$

The two opposing pressures, osmotic and electrolytic solution, are thus equalized for each of the two metals; hence an electro-motive force applied to the alloy as anode will cause equal amounts of copper and zinc to be dissolved. Such a mixture would be made if a saturated solution of a zinc salt were in contact with a plate of the 50 per cent. alloy, and the alloy, when made the anode, would dissolve evenly. It is necessary now, however, to consider the cathode upon which the metal will be precipitated. Here we will not get, at any current density, the alloy we expect so that the relation between the zinc and copper ions in the solution will change, and consequently the two constituents will then be dissolved from the anode in another ratio. *For the deposition of any alloy, then, we see that it is necessary that the following conditions be fulfilled: 1. That the solution have such an ionic concentration of the two metals that the correct amount of each constituent dissolves from the anode; i. e., that the alloy dissolves as such. 2. That the correct alloy separates at the cathode, so that the composition of the liquid is not altered in such a way that the first condition is unfulfilled.* With alloys of copper and zinc we see that, for simple salt solutions, the first condition can be fulfilled, but the second can not.

A solution from which brass may be deposited and which will retain this power, by dissolving the correct proportions of copper and zinc from the anode, must have the following properties, which are self-evident from what has already been said: *1. It must contain ions of zinc and copper in such a proportion that 30 per cent. of zinc, and 70 per cent. of copper will be dissolved from the anode; i.e.,* $\dfrac{P}{p} : \dfrac{P'}{p'} :: 30 : 70$. *2. It must contain complex ions of zinc and copper, from which these metals may be separated.* These are necessary, for we have seen that simple metallic ions cause changes in the composition of the solution and thus vary the composition of the alloy dissolved. There is also less work needed to separate metals from complex ions than from simple ones. *3. For economy, the maximum concentration of copper*

*ions should be as small as possible in order that copper may be
separated easily from the anode.*

All these conditions are fulfilled by a solution of the mixed
salts of copper and zinc in potassium cyanide solution. We have
first an extremely small concentration of zinc and copper ions.
The absolute value of the concentration of copper ions can be
appreciated from the consideration of the following experiment:
When a solution of potassium cyanide is poured upon the copper
side of a Daniell cell, the poles are reversed; *i. e.*, copper becomes
the negative pole. In order to do this, it is necessary that

$$\frac{P}{p} \, (\text{ZnSO}_4) < \frac{P'}{p'} \, (\text{CuSO}_4 \text{ in KCN});$$

i. e., that the value of p becomes so small that $P'(= 4.8 \times 10^{-20})$
exceeds it and copper goes into solution. We have the complex
ions $\overline{\overline{\text{Zn(CN)}}}_4$ and $\overline{\overline{\text{Cu(CN)}}}_4$, from which zinc and copper may be
deposited in varying proportions according to the current
density, for zinc needs a greater current density than copper.
In other words from our theoretical knowledge we can predict
that such a solution would serve our purpose.

It would seem necessary, next, to find just what proportion of
zinc and copper salt should be present in the cyanide solution,
to give the correct ratio of ions. This, however, is not necessary,
as is shown by the following consideration, for this ratio adjusts
itself automatically during the reaction. In practice, at times,
a bath is made up as follows: A solution of potassium cyanide
is electrolyzed, at the correct density to deposit brass, for several
hours with brass electrodes, the liquid being drawn off and used
as the bath. From the brass anode ions of zinc and copper ions
are given off into the solution forming the salts $K_2\text{ZnCN}_4$ and
$K_2\text{CuCN}_4$. These salts dissociate, to a very large extent, into
$\overset{+}{2\text{K}}$ and $\overline{\overline{\text{MCN}}}_4$, where M represents either copper or zinc. There
is also a further dissociation, to a very slight degree, into $\overline{2\text{K}}$,
$\overset{++}{\text{M}}$ and $\overline{4\text{CN}}$. The zinc, on account of its high electrolytic solu-
tion pressure, will dissolve to a greater extent than the copper,
so that there will be more ions of $\overline{\overline{\text{ZnCN}}}_4$ than of $\overline{\overline{\text{CuCN}}}_4$. Only
30 parts of zinc, however, at this current density can separate to

every 70 parts of copper so that there is also a concentration of $\overline{Zn}\overline{CN}_4$ ions on the cathode side; this takes place after hydrogen has been given off for a time. The equilibrium in the solution is fixed by certain equations. By these only a certain amount of free zinc ions can exist in the solution, all over this amount being transformed into $\overline{Zn}\overline{CN}_4$, and of this latter a relatively small portion only can separate at the cathode. For this reason when the solution becomes saturated with $\overline{Zn}\overline{CN}_4$ ions, it exerts the same counter pressure with its free zinc ions as it would if the solution were saturated with zinc ions, since any more zinc ions would supersaturate the solution. For this reason zinc can only dissolve to the same amount in which it separates.

The copper ions in the solution are so few that, as before observed, the metal acts as though it possessed a high electrolytic solution pressure. There is a larger number of $\overline{Cu}\overline{CN}_4$ ions and since these break up and separate copper to a greater extent than those of $\overline{Zn}\overline{CN}_4$ separate zinc, and since the solution never becomes saturated with them, the terms $\dfrac{P}{p}$ and $\dfrac{P'}{p'}$ become of the same order, and are related as 30 : 70. It is thus seen that the regulation of the relative concentration of zinc and copper dissolved is automatic and depends upon the current density which regulates the ratio deposited. In few words we may sum up the behavior as follows: The solution is saturated with zinc, since no more can exist either as Zn or as $\overline{Zn}\overline{CN}_4$, except as Zn from $\overline{Zn}\overline{CN}_4$ separates. The relation $\dfrac{P'}{p'}$ is increased by the exceedingly small value of p' so that ions of copper can form, but as they form they separate on the other side, removing the saturated condition with respect to zinc, so that the correct relative amount of this also can separate and dissolve, etc.

Another method consists in dissolving equal weights of copper and zinc salts in a solution of potassium cyanide. The action, of course, is exactly similar to that given above for potassium cyanide solution alone, so that it will not be necessary for us to consider it. '

It is thus possible from purely theoretical knowledge, and a few appropriate simple experiments to find just what solutions must be used for baths for the deposition of any alloy. The contrast between this method and the old empirical one of trying all combinations until a lucky hit is made, the true reasons for which are unknown, is striking, but it is just what is being experienced to-day in all branches of chemistry by the application of theory to practice. The other ingredients which are used in the baths are to produce a fine smooth coating and have nothing to do with the theory of the method. Of course there are other solutions which behave just as the double cyanides do, but as the theory is the same, the only idea of a change would be for economy and that is a question for the technical side of the subject. Such another solution which is used is made by dissolving zinc and copper salts in an excess of ammonia. Here we have just as before Zn and Cu ions, and also complex ones which behave just as $\overline{Cu}\overline{CN}_4$ and $\overline{Zn}\overline{CN}_4$.

Another liquid which causes copper to act as a metal of high electrolytic solution pressure is a solution of potassium sulphide.

THE DETERMINATION OF SULPHUR IN BITUMENS.

BY A. C. LANGMUIR.

IN the September number of this Journal, S. F. and H. E. Peckham criticize a paper by E. H. Hodgson which appeared in November, 1898, and describe, in some detail, their own method slightly modified.

The authors claim for their method that it is "simple, reasonably rapid and accurate" and state that it is "susceptible of great accuracy, if *conducted with care*. It requires great care from the beginning to the end. Mr. Hodgson's results do not indicate great care,—they are not sufficiently concordant."

It is but fair to Mr. Hodgson to call attention to certain features in Messrs. Peckham's method which cannot inspire chemists with confidence and which may possibly indicate that the authors themselves have not bestowed on their method the great care which they miss in Mr. Hodgson's work.

A brief review of the method is necessary: Approximately

0.5 gram of the bitumen is fused with 30 grams of a mixture of equal parts of sodium carbonate and potassium nitrate in a platinum crucible. The crucible contents are dissolved in water, hydrochloric acid is added, and the silica is separated by evaporation on the water-bath and dehydration. After taking up with hydrochloric acid and water the silica is filtered and the filtrate is rendered alkaline with ammonia to precipitate iron and alumina. The excess of ammonia is removed by boiling, and the iron and aluminum are filtered off. The lime is removed by ammonium oxalate and in the filtrate from the latter, now free from silica, alumina, iron and lime, the sulphuric acid is precipitated by the usual method. The convenience of esti- mating the mineral constituents in the same solution with the sulphuric acid is noted. In our opinion, what is gained in convenience, if any, by this method, is lost in accuracy.

In some bitumens the amount of sulphur is very low. In others the proportion of mineral matter is so high that very con- siderable amounts of iron, alumina, or lime may be met in the course of the analysis.

If the above method is to be generally applied the following objections should first be answered:

In the course of the fusion with alkaline carbonate and nitrate there is danger of the absorption of sulphuric acid produced by the burning gas. Any error from this cause would be especially noticed in the analysis of bitumens low in sulphur. An alcohol lamp should be used or the crucible should rest in a hole cut in asbestos board to protect the fusion from the access of the products of combustion.

Messrs. Peckham have not given us details sufficient to enable us to decide whether they have made use of these necessary pre- cautions. Several chemists have called attention to this danger.[1]

In the slow evaporation of the fusion on the water-bath there is again a possible source of error in the absorption of sulphur, if, as is often the case, the bath is heated by gas.

Hillebrand[2] finds that the sulphur introduced in this way in the analysis of silicate rocks is frequently as much as the entire sulphur present. The writer's own experience has confirmed

[1] Price : *J. Chem. Soc.*, London, **2**, 51; Fresenius: *Ztschr. anal. Chem.*, **16**, 339; Lunge : *J. prakt. Chem.*, **40**, 239

[2] Bull. U. S. Geol. Survey, **148**, 1897.

this statement entirely and rather than dehydrate for silica we have precipitated the sulphuric acid directly in the acidulated aqueous solution of the fusion. We have never found any silica in the barium sulphate so obtained, but if its presence is feared it may be readily removed with a little hydrofluoric and sulphuric acids.

How considerable the contamination of the evaporating solution may be is plain from the experiment of E. von Meyer[1] who found, after evaporating 2 liters of distilled water down to 50 cc. during six hours on the water-bath, the equivalent of 0.0426 gram barium sulphate present.

A third objection and the most serious of all is against the separation of iron and alumina by boiling out the excess of ammonia. It is well known that iron can only be precipitated free from sulphur in a solution containing the latter by adding a distinct excess of ammonia to the moderately warm solution, heating a few minutes on the water-bath and filtering immediately. Only in this way can the formation of insoluble basic sulphates be prevented. Boiling the solution is, of all things, to be avoided. Lunge[2] states that correct results can only be obtained by adhering strictly to this procedure and that deviations lead to serious errors.

The check analyses made by the authors do not controvert the criticisms just made as the asphalt analyzed was said to be very pure and was presumably free from mineral matter.

Finally, in view of the recognized tendency of barium sulphate to drag down with it other mineral constituents of the solution and barium salts of other acids present, what must be said of precipitating sulphuric acid in the presence of ammonium oxalate and the alkaline chlorides from 30 grams of mixed carbonate and nitrate?

Our preference is given to Eschka's method following the details as described by Heath.[3] The Eschka method is admittedly the best for the determination of sulphur in bituminous coals. The problem here is a very similar one. In addition to its convenience and rapidity the Eschka method has the

[1] *J. prakt. Chem.*, 42, 267; see also Gunning : *Ztschr. anal. Chem.*, 7, 480; Alex : *Ibid.*, 10, 246; Wagner : *Ibid.*, 20, 323; Lieben : *Ibid.*, 32, 214; Privozink : *Ber. d. chem. Ges.*, 28, 2200.

[2] *Chem. News*, 71, 132; *J. prakt. Chem.*, 40, 239.

[3] This Journal, 20, 630.

advantage of leaving the iron, lime, and alumina insoluble at the start and only a small quantity of alkali is introduced into the analysis.

As for the mineral constituents they are better determined on a separate portion. Their accurate determination is made all the more difficult by the presence of an excessive amount of alkali metals as in Peckham's method.

Our practice has been to heat the asphalt at a low temperature in a platinum dish, slowly driving off the volatile constituents in such a way that the asphalt does not burn. At the end the temperature may be raised and the remaining organic matter burned without danger of loss.

The ash is extracted with hydrochloric acid and any insoluble residue fused with a small amount of the mixed carbonates. The solution of the fusion in hydrochloric acid is added to the other and the analysis proceeded with as usual. In this way the quantity of alkaline salts is reduced to a minimum.

Time is actually lost by determining the metals and sulphur in one portion as the determination of the latter must wait until the metals have been separated.

In all but two of the asphalt analyses of Dr. Day, as quoted by Messrs. Peckham, the decimal point is misplaced, making the per cent. sulphur far less than it should be.

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THE DETERMINATION OF NICKEL IN NICKEL ORES.

BY A. C. LANGMUIR.

GEORGE WILLIAM SARGENT'S paper on the "Determination of Nickel in Nickel-Steel" in the October number of this Journal, prompts me to publish a somewhat similar method for the determination of nickel in its ores, which has been in use in this laboratory for several months with excellent results. It is particularly advantageous in all cases in which a relatively small quantity of nickel is to be separated from a large amount of iron and surpasses all other methods such as the basic acetate, basic carbonate, or ammonia separations.

One gram of the ore is covered in a No. 2 Griffin's beaker

with 15 cc. concentrated nitric acid. One or two cc. of liquid bromine is added and the contents are gently heated until the bromine is expelled. The solution is then boiled down almost to dryness. Bromine in combination with nitric acid effects so thorough an oxidation that no sulphur bead can form. This reaction may also be applied in the analysis of copper mattes, where it is often necessary to filter off the sulphur bead which usually forms after the treatment with nitric acid and to roast it to recover the small amount of undecomposed sulphide which it invariably contains. The addition of bromine renders this extra operation entirely unnecessary.

After expelling the excess of nitric acid, about 50 cc. of concentrated hydrochloric acid are to be added and the solution slowly boiled down to 5 cc. The nitric acid is expelled and any residue carrying nickel and insoluble in nitric acid is brought into solution—at least in the ores handled by us.

Dilute to 250 cc. with hot water and pass hydrogen sulphide to remove copper, etc. Filter and boil the filtrate to expel hydrogen sulphide. Oxidize the ferrous iron by adding nitric acid to the boiling solution, drop by drop, carefully avoiding any excess. Cool slightly and add ammonia until distinctly alkaline. Filter and wash twice with hot water, catching the filtrate which will contain the bulk of the nickel in a large casserole and boil it down while the remaining operations are being performed.

Dissolve the ferric hydrate which carries a considerable amount of nickel in warm dilute hydrochloric acid. Wash into a casserole and boil down rapidly until pasty. Add about 10 cc. of hydrochloric acid (1.10 sp. gr.), warm slightly, rinse into a 250 cc. separating funnel with acid of the same strength, keeping the volume down to 50 cc., if possible, and cool thoroughly. Add now 40 cc. of C. P. ether and agitate vigorously at least five minutes. Invert the funnel occasionally and open the stop-cock cautiously to lower the pressure. The ferric chloride gradually dissolves in the ether leaving the nickel, aluminum, and any cobalt or manganese in the aqueous solution as chlorides.

The first solution obtained by boiling down the nitric acid residue with 50 cc. of hydrochloric acid cannot be profitably treated by the ether separation. On account of the sulphuric

acid formed by the oxidation of the sulphur, the removal of the iron by ether is far from complete. The sulphuric acid must be separated from the iron by an ammonia separation so that a solution containing only chlorides may be obtained. There is almost always some slight loss of solution in the treatment with ether in the separatory funnel, but any error from this source becomes negligible if the bulk of the nickel is first separated by ammonia.

After agitating, the funnel is allowed to stand a few minutes and the water solution is drawn off into a second funnel. The ether solution is washed twice with a few cc. of hydrochloric acid (sp. gr. 1.10), the washings being caught in the second funnel. Mr. Sargent contents himself with one ether treatment but we have always found it advisable to remove the iron still remaining with the nickel by a second agitation with 40 cc. of ether. The second operation is carried out in the same way as the first.

The aqueous solution and washings are run into a beaker, the dissolved ether is expelled by boiling, bromine water is added until the solution is strongly colored, and the iron, aluminum and any manganese present are separated by adding ammonia to alkalinity and boiling. If the ether treatment has been properly carried out, a mere trace of iron remains with the nickel and the precipitate may be caught on a 9 cm. paper. The precipitate obtained as above is dissolved in a little hydrochloric acid, bromine is added, and the precipitation with ammonia is repeated. The combined filtrates and washings are added to the casserole containing the now concentrated filtrate from the first ferric hydrate precipitate. The contents of the casserole which now contain all of the nickel in the ore are concentrated to 100 cc. or until ammonium chloride begins to separate. Fifty cc. of concentrated nitric acid are added and the solution is slowly boiled down almost to dryness. In this way the ammonium chloride is entirely destroyed. Ammonium nitrate is unchanged; hence the necessity for avoiding an excess in the oxidation of the ferrous iron. We are now able to concentrate the solution to a volume of a few cc. without the separation of any salts. Ten cc. of concentrated sulphuric acid are added and the casserole heated until dense fumes appear and the nitric acid is entirely

expelled. After cooling, dilute with 100 cc. cold water, boil, rinse into the high beaker used for electrolytic determinations, neutralize with ammonia, and add 25 cc. in excess. Dilute to 200 to 250 cc., insert the spiral and the weighed platinum cylinder, and electrolyze with a strong current,—we have used 1.2 amperes. The precipitation of the nickel is generally complete within three hours.

The separation of iron and nickel by ether has not as yet been used in the analysis of nickel ores, or mattes. It is unequaled for cleanliness, rapidity, and accuracy, and deserves the first place among the many methods proposed for the separation of iron and nickel.

The ammonia separation has proved particularly untrustworthy in our hands. Three and even four separations fail to remove the nickel, even if the acid solution containing the iron be poured into water containing an excess of ammonia.

The ready means afforded for destroying almost unlimited quantities of ammonium chloride by boiling down with an excess of nitric acid is not new, having been suggested long ago by Lawrence Smith in connection with his well-known method for alkali determinations. Yet it has been strangely neglected and we believe has never been used in the analysis of nickel ores, where it is particularly useful as it enables us to avoid the troublesome and inaccurate separation of the nickel as sulphide.

The solutions to be tested for nickel, ordinarily obtained in analysis, are choked with ammonium chloride, which prevents the concentration of the solution and necessitates the preliminary separation of the nickel from a dilute solution of sulphide. The difficulties in the way of precipitating and washing nickel sulphide without loss in the filtrate or washings are too well-known to need repetition.

In some analyses made by the author before his adoption of the ether method it was necessary to test for traces of nickel in several samples of steel. At least 5 grams had to be taken and the ammonium chloride accumulating in the filtrates from the ammonia separations of the iron was so large in amount that concentration to a bulk in which ammonium sulphide would reveal nickel was out of the question. But by boiling down slowly, with copious additions of nitric acid, it was possible to

destroy all the ammonium chloride and to finally test for nickel in a volume of some 15 cc. under ideal conditions.

The ether separation, as based on the solubility of ferric chloride in ether under the above conditions is, in all probability, not restricted to the determination of nickel or aluminum, but may possibly be applied in the separation of small amounts of zinc from iron. The separation of uranium and iron by ammonium carbonate and sulphide is far from satisfactory if the uranium be small in amount. Possibly in this case as well, the ether treatment may result in a decided improvement.

LABORATORY OF RICKETTS AND BANKS,
        NEW YORK.

LABORATORY METHOD FOR THE CONTINUOUS AND UNIFORM GENERATION OF ACETYLENE, AND FOR ITS PURIFICATION.

BY J. A. MATHEWS.

FOR most purposes in which it is desired to employ a stream of acetylene, no purification is necessary, provided the gas has been properly generated from the usual quality of commercial carbide now being produced. Analyses from various sources show that the impurities in acetylene from this source rarely amount to 1 per cent. and a good part of this is likely to be nitrogen. The combined amounts of hydrogen sulphide, hydrogen phosphide, and ammonia seldom exceed 0.2 per cent. In order that the amount of impurities may be as small as possible it is necessary that the gas be produced in the cold. This cannot be done when water is allowed to drip slowly upon the carbide, and furthermore this method causes the gas to be given off spasmodically and the lime residue often bubbles or froths to such an extent that solid matter in considerable amounts may be carried over with the gas. In obviating all these difficulties the following method has proved successful.

The fragments of calcium carbide are placed in a wide-mouthed bottle. They may, with advantage, be suspended in a basket of coarse wire netting, which will keep the carbide away from the

lime residue, and also allow it to be withdrawn at any time. The carbide is covered with an abundance of absolute or 95 per cent. alcohol, and the bottle closed with a two-hole stopper. Through one hole water can be led from a reservoir bottle, and in the other an outflow tube is fitted. If 95 per cent. alcohol is used, the water therein serves to start the generation of acetylene and to expel the air from the apparatus. If, now, water be added drop by drop it comes slowly into contact with the carbide and a steady production of acetylene results. Unless the amount of alcohol present is very small and the rate of generation very rapid, no material rise in temperature ensues. After the addition of water has been stopped, the evolution of gas may be allowed to proceed until the bubbling ceases; the alcohol may then be decanted from the residue and distilled, and, rejecting the first few cubic centimeters, the rest of the distillate will be nearly absolute alcohol.

If it is desired to purify the acetylene, any one or more of several methods may be employed. No single purifying agent which has as yet been advocated, meets all the requirements. For general convenience and thoroughness the following combination of methods is suggested:

The acetylene generated as described above is passed into a solution of 15.6 parts of crystallized copper sulphate in 100 parts of water, to which is added 5 parts of dilute sulphuric acid,[1] 1 volume of sulphuric acid to 4 volumes of water. This solution, besides retaining any vapor of alcohol and also the ammonia and hydrogen sulphide, is especially useful for absorbing hydrogen phosphide. As an additional safeguard the acetylene is next passed through one or two towers filled with coarse bits of pumice stone which have been saturated with an acetic or sulphuric acid solution of chromic acid;[2] or, in place of a second tower, a strong sulphuric acid solution of chromic acid may be used. By this means any of the three chief impurities, which might escape absorption in the copper sulphate solution, will be completely oxidized. A small amount of these purifying materials will serve for a large volume of gas, and the acetylene should issue both dry and pure and possessing a faint and agreeable odor.

[1] Hempel and Kahl : *Ztschr. angew. Chem.*, **53**, 1898.
[2] Ullmann : *J. für. Gasbeleucht*, **42**, 198, 374 (1899).

A return of the strong, irritating odor indicates that the purifiers have become exhausted.

The purification of acetylene by means of moist chloride of lime or sodium hypochlorite, as suggested by Odernheimer[1] and Lunge[2] or as modified by Wolff[3], is impracticable because of the instability of the solutions and because chlorine and chlorination products of acetylene are produced, which must then be removed by lime. Frank's method,[4] using strongly acid solutions of copper or iron chloride, does not seem very efficient, nor is the employment of bromine as a purifier convenient for laboratory use. The combination of Hempel's and Ullmann's methods seems to meet all the requirements and is easily and conveniently arranged.

THE CARBIDE OF GOLD.

BY J. A. MATHEWS AND L. L. WATTERS.

EXPLOSIVE compounds resulting from the action of acetylene or coal-gas upon alkaline solutions of cuprous, argentous and mercuric salts have been known for many years. These compounds are for the most part flocculent precipitates which retain water with more or less tenacity, and at temperatures which will render them anhydrous they are apt to explode violently. The earlier investigators of these acetylides did not recognize them as true carbides and their analyses show the presence of hydrogen and oxygen, which are reported as constituent atoms of the molecule. Berthelot,[5] who did a great deal of work upon acetylene derivatives, speaks of copper acetylide as "cupro-acetyloxide," and gives it the formula $(C_2Cu_2H)_2O$. Reboul[6] gives silver acetylide as $(C_2HAg)_2 + Ag_2O$ and Blochmann[7] gives respectively, $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$. All of these might better

1 Chem. Ztg., 22, 21.

2 Ztschr. angew. Chem., 651 (1897).

3 Chem. Ztg., 22, 281; Wolff treats the gas first to remove ammonia and then with hypochlorite, thus eliminating the danger of forming nitrogen chloride, which he says is possible.

4 Ztschr angew. Chem., 1050 (1898).

5 Ann. chim. phys. [4], 9, 425.

6 Compt. rend., 54, 1229.

7 Ann. Chem. (Liebig), 173, 176, 177.

be written C_2Cu_2 or C_2Ag_2 plus more or less water. Miasnikoff[1] gives silver acetylide as $C_2H_2Ag_2$. Keiser[2] showed, however, that when properly dried these two acetylides are simply C_2Ag_2 and C_2Cu_2, and later[3] produced mercuric acetylide, HgC_2, which is also hydrated at the time of its formation.

Berthelot[4] seems to be authority for the statement which appears in a number of old chemical works, but for which these do not give him credit, that by passing acetylene through aurous thiosulphate, a yellow explosive precipitate is formed. He gives no analyses of the product and does not give any suggestions as to its probable constitution.

We have recently investigated this interesting compound, which proves to be analogous to the copper and silver compounds, its formula being aurous carbide, Au_2C_2.

In the preparation of aurous sodium thiosulphate we followed the method of Fordos and Gélis.[5] Pure auric chloride was dissolved in 50 parts of water; 3.2 parts of sodium thiosulphate were dissolved in the same amount of water. The solution of gold was added to the thiosulphate very slowly and with constant stirring. A slight odor of sulphur dioxide was noticed and a little sulphur separated.

The solution was filtered and the sodium aurous thiosulphate was precipitated with absolute alcohol. It was not recrystallized. The principal reaction is said to be

$$8Na_2S_2O_3 + 2AuCl_3 = 2Na_3Au(S_2O_3)_2 + 2Na_2S_4O_6 + 6NaCl.$$
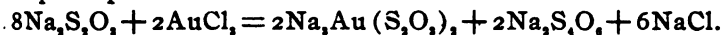
This compound forms a colorless precipitate, very soluble in water but insoluble in alcohol. To form aurous carbide an aqueous solution of the sodium aurous thiosulphate is made strongly alkaline with ammonia and a slow stream of acetylene passed through. The solution remains colorless for a short time and then becomes yellow and finally a yellow flocculent precipitate appears. In this respect it differs from silver and copper carbides, which form almost instantly and hence are used to test for the presence of minute quantities of acetylene. The precipitate is filtered off, washed with water and alcohol and dried in a desiccator over sulphuric acid.

[1] *Ann. Chem.* (Liebig), 118, 330.
[2] *Am. Chem. J.*, 14, 285.
[3] *Ibid.*, 15, 535.
[4] *Ann. chim. phys.* [4], 9, 425.
[5] *Ibid.*, [3], 13, 394, 1845.

Properties.—When· thoroughly dried, the carbide of gold is highly explosive either upon rapid heating, by a blow or even by brushing with a camel's hair brush. The explosion generates sufficient heat to produce flame and the gold· is left in an extremely finely divided condition and black. Carbide of gold is easily decomposed by hydrochloric acid giving acetylene and leaving a black residue of aurous chloride. The presence of. acetylene was shown by passing it into ammoniacal silver nitrate, in which it produced silver acetylide. The aurous chloride was tested by boiling, which gave auric chloride and metallic gold. By boiling. gold carbide with water it is decomposed into its constituents, no acetylene being produced. Cupric sulphate and neutral ferric chloride do not decompose it in the cold; when anhydrous it becomes darker in color and of a brown tint and if heated very gradually decomposes without explosion. This fact was made use.of in the determination of gold. The sample to be analyzed was heated in the air-bath very slowly until a temperature of 180° to 200° was indicated, and then ignited in the flame of a Bunsen burner. The black mass becomes yellow by the burning off of the carbon and annealing of the gold. The analyses resulted as follows:

	Weight of sample.	Gold found.	Gold. Per cent.	Theory for Au_2C_2.
I	0.029	0.0273	94.14	94.25
II	0.0174	0.0164	94.25	94.25

One sample of aurous carbide after two days in the desiccator lost no weight at 100° C. nor was loss experienced on renewed heating up to 120° C. Another· sample that had not stood so long over sulphuric acid lost 0.0004 gram at 100°. By rapid heating in the air-bath explosions were obtained at various temperatures from 83° to 157° C. No attempt was made to secure especially uniform heat at all parts of the air-bath, but the thermometer bulb was in all cases very close to the dish containing the explosive compound. It seems then that the rate of heating has most to do with effecting the decomposition of gold acetylide. The violence of the explosion was shown by several unexpected explosions. In one case about 15 or 20 milligrams of the substance were on a watch-glass. In trying to remove a small fragment with the point of a knife, the whole

mass exploded with a sharp report and the watch-glass was broken into a score of pieces. In another instance while brushing some of the carbide from a filter-paper with a camel's hair brush into a dish, the particles adhering to the paper exploded with a loud report anu flame and the filter-paper was badly torn but the bulk of the material, which was not over an inch or two away,'was not exploded by the concussion. The same fact was noted in the first explosion above in which case the watch-glass was standing beside a crucible containing quite a large amount of dry gold carbide.

No other aurous solutions were tested with a view to obtaining gold carbide. From auric chloride in aqueous solution metallic gold is precipitated by acetylene.

A solution of auric chloride made alkaline with potassium hydroxide does not give a precipitate under similar conditions, nor does an aqueous or ammoniacal solution of potassium auric cyanide give a precipitate when acetylene is passed into it.

THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.

BY F. P. VENABLE.

IN a recent number of this Journal[1] Whitney has reported further work upon this problem and at the same time criticized an article by Venable and Miller which had previously appeared upon the same subject.[2] As Mr Miller is no longer at work with me and I was, in the main, responsible, for the presentation and discussion with which Dr. Whitney finds fault, my name appears alone in this reply.

Whatever disinclination I may have felt to accept as final the previous efforts at determining the presence of free sulphuric acid in the green solutions, I can have none as to this recent admirable and conclusive direct determination of the acid by Whitney. It is, of course, of little importance to explain why an opinion was formed, unless truth is advanced by such explanation. I shall therefore only refer to two or three of the facts stated by Whitney as sufficient to convince one that free sul-

1 This Journal, 21, 1075-1084.
2 Ibid., 20, 484-496.

phuric acid is present.   I do this because I cannot verify them as facts.

1. Dr. Whitney states that the green solutions are acid to the usual indicators.   We could draw no conclusions as to the difference between the solutions from this because both violet and green solutions are thus acid.   This statement was made by us in the original article and has been carefully verified by me since reading Whitney's article.   It is also supported by the experiments of Baubigny and Pechard.   Furthermore, the mere fact that barium chloride is prevented from precipitating all of the sulphuric acid in the green solution cannot be taken as proving the presence of free sulphuric acid.

2. Whitney cites Recoura as stating that the " distillation of the green solution results in an acid distillate, while the violet salt may be heated above 100°C. without loss of acid."   My experiments failed to verify this.   I took 15 grams of the alum and dissolved it in 200 cc. of distilled water.   This was then carefully distilled from an ordinary distilling flask connected with a condenser and the distillate treated in successive portions of 50 and 25 cc. until only about 25 cc. were left, without finding any acid. Beyond this point the temperature began to rise, portions splashed upon the sides became overheated, and acid distilled over.   This was repeated with chromium sulphate with the same result.   It was also repeated with ordinary potash alum with the same result.   As the solution became very concentrated the temperature rose, portions were splashed upon the hot sides and acid distilled over.   Lastly, it was repeated with 5 cc. of sulphuric acid in 200 cc. of water and no acid distilled over until most of the water had been driven off and the temperature had risen above 100°C.   Manifestly this experiment of Recoura's can throw no light upon the presence or absence of free acid.

3. Krüger's statement that alcohol poured in a layer over the green solution takes up acid (something that gives an acid reaction) from the solution is only part of the truth for alcohol will do precisely the same thing when poured over the violet solution. In the course of a few hours the reaction is quite perceptible from both solutions.   There is no change apparent in the color of the violet solution after four or five days' standing under the layer of alcohol.

After weighing the evidence then at hand I reached the conclusion that a satisfactory explanation of the change could scarcely be deduced from these and the other experiments.

And they did not seem to me to justify the construction of an equation and an elaborate formula for a hypothetical substance which was assumed to cause the green coloration, even if the presence of the free acid should be granted.

The exception is well taken by Whitney to our experiment with the decinormal solution of ammonia and explains a result which greatly puzzled us in the interpretation of our later work. We scarcely knew what value to attach to the experiment and so merely stated that "these experiments therefore agree with those of Baubigny and Pechard, but are at variance with the conclusions of the other authors mentioned." The agreement was, of course, only to the extent that "both solutions are acid" and that was all that was claimed for the experiment.

It seemed to us necessary to get under hand for analysis the body which gave the green coloration before any formula could be established for it.   We therefore abandoned what we styled "indirect methods giving results capable of other explanations." We thought it more material to secure this body than to settle the question as to whether free acid or an acid sulphate was formed.   Certainly any other line of research would always leave the body in question hypothetical.   Hence in the latter part of the paper[1] the sentence occurs, "as the alcohol left is decidedly acid it must contain either free acid or an acid sulphate" and there was no further effort at settling this point.

The method which most commended itself to us for securing this compound was precipitation by means of alcohol.   In this precipitate, in the case of the alum, we obtained the potassium sulphate along with the chromium compound and this blinded us to the true formula.   A recalculation of the results of Mr. Miller's analyses, eliminating the potassium sulphate, and taking the mean of the experiments, gives as the ratio of the chromium to SO_4, 18.23 : 41.62.   Now the ratio, calculated for the formula $Cr_4O.(SO_4)_4.SO_4$, is 18.23 : 41.99.   Having then the direct determination of the free sulphuric acid from Whitney's last experiments and the gravimetric determination of the chromium

[1] This Journal, 20, 496.

and SO, in the basic chromium sulphate from Miller's analysis, there can no longer be any reason for not accepting the equation given for the change :

$$2K_2SO_4.Cr_2(SO_4)_3 + H_2O = 2K_2SO_4 + Cr_2O(SO_4)_2.SO_4 + H_2SO_4.$$

The conclusion drawn in the article by Miller and myself was conservative and still stands ; namely, that the color of the green solutions was due to the formation of basic salts of chromium, green and uncrystallizable, thus confirming the explanation first suggested by Berzelius. To this must now be added that this formation is accompanied by the liberation of a portion of the combined acid, in the case of the alum corresponding to one-half of the total.

ON THE DECOMPOSITION OF NICKEL CARBONYL IN SOLUTION.

BY VICTOR LENHER AND HERMANN A. LOOS.

IT has been shown by Berthelot that nickel carbonyl in contact with moisture suffers decompositions of a more or less complex character. When nickel carbonyl is mixed with water according to Berthelot[1] there is formed a green compound which consists of hydrate of the oxide free from carbon. A portion of the nickel carbonyl at the same time escapes and is oxidized in moist air to a whitish compound. This same white compound Berthelot prepared in larger quantity by the slow oxidation with air and found it to contain 5.3 per cent. carbon, 53.3 per cent. nickel oxide (NiO), and 40.1 per cent. water.

Mond[2] considers the green body formed when nickel carbonyl is exposed to damp air to be a carbonate of nickel of varying composition.

The deportment of nickel carbonyl in solution is different from that in the pure condition or as a gas, as is seen, for example, from the fact, that it will decompose in solution at 60°, whereas in the gaseous condition, it will not decompose until about 150°.

[1] *Compt. rend.*, 112, 1343 ; 113, 679.
[2] *Chem. News*, 64, 108 ; also *J. Soc. Chem. Ind.*, 11, 750.

In gaseous condition, heat decomposes it simply, into nickel and carbon monoxide.

$$Ni(CO)_4 = Ni + 4CO.$$
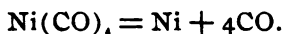
In solution the action takes a different form and may be represented as follows :

$$Ni(CO)_4 = Ni + 2C + 2CO_2.$$
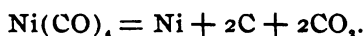
It would not be surprising then to find that the solution would act differently than the pure substance, under the action of moisture or oxidation.

While working with nickel carbonyl dissolved in various organic solvents, such as chloroform, benzene, toluene, etc., it was found that the solutions on standing suffer decomposition with the formation of a green precipitate ; this was probably due to the presence of more or less moisture, either in the solvent or in the surrounding atmosphere. That the precipitate is produced by the action of moisture is evidenced by the fact that the decomposition is more rapid when the solution is exposed to the air and still more rapid when moist air is bubbled through the solution.

A solution of nickel carbonyl will, after standing, suffer decomposition with the formation of a green to a brown gelatinous precipitate. In appearance, this precipitate is similar to that obtained by the action of water or moisture on pure liquid nickel carbonyl.

The precipitate formed from various solvents has been studied with a view of determining if possible its composition. The substance is evidently of very complex nature and is undoubtedly an oxidation product. When a solution of nickel carbonyl in acetone or chloroform is allowed to stand, a green gelatinous precipitate forms in a few hours. After a greater length of time the precipitation becomes complete, and on filtration, no nickel can be found in solution. This same decomposition takes place but more slowly in benzene, toluene, and methyl alcohol. The precipitate is colored light green to dark brown according to the solvent used, and according to the small amount of iron carbonyl which frequently contaminates the nickel carbonyl. The deportment of the solution in ethyl alcohol is peculiar. If this solution is mixed with an equal volume of water, a clear solution is

first obtained, but in a few minutes, it gelatinizes to a green translucent mass. This substance settles very slowly. On ·filtering off the precipitates and carefully drying, all assume a greenish color. Examination of this precipitate indicates that it is a decomposition product which contains nickel carbonyl and nickel hydroxide.

Analyses of the substance obtained from toluene gave the following results :

	Calculated for $Ni(CO)_4.2Ni(OH)_2.4H_2O$.	Found. I,	II.
Carbon	11.19	11.66	11.38
Hydrogen	2.80	2.95	2.97
Nickel	41.26	42.82	42.68

As different samples gave results which differed slightly, it appears that the composition of the substance varies slightly as is apt to be the case in an oxidation product. A precipitate from benzene was found to contain 42.09 per cent. of nickel, while one from chloroform contained 42.81 per cent.

The precipitate carbonizes with sulphuric acid while with dilute acids carbon dioxide is evolved. Sodium or potassium hydroxide attacks the precipitate and apparently removes a portion, since after treatment with one of these alkalies and thoroughly washing, acids will no longer produce effervescence. Potassium iodide is without action ; potassium cyanide dissolves it to a brown solution. It is insoluble in chloroform, benzene, toluene, petroleum ether, alcohol, acetone, methyl alcohol, or ether. Ammonium sulphide converts it to the black sulphide of nickel. Although the formula calculated for comparison with the analyses does not account for the evolution of carbon dioxide with an acid, yet this can be explained by the fact that carbon dioxide is invariably a result of the decomposition of nickel carbonyl in solution.

ERRATUM.

In the December issue (1899), on page 1145, in the fourth line of table, for "calcium chloride" read "chloride of lime (bleaching powder)."

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SUBSTITUTES FOR HYDROCHLORIC ACID IN TESTING CARBONATES.

BY JOSEPH W. RICHARDS AND NORMAN S. POWELL.

THE following experiments were undertaken in the hope of finding a satisfactory substitute for hydrochloric acid in producing effervescence with natural carbonates. It is well-known that hydrochloric acid is difficult to carry in a portable set of apparatus, and while it is entirely satisfactory to use it in the laboratory, yet it would be very desirable to have some solid material to replace it in a portable testing outfit.

The materials tested as substitutes were potassium acid sulphate, citric acid, tartaric acid, and oxalic acid. These were made into solutions of the strength of 4 parts of water to 1 part of salt or acid, or 20 per cent. solutions. This would correspond roughly to dissolving a piece the size of a pea in 1 cc. of water. Such a solution, in a test-tube, makes a suitable reagent. Oxalic acid, however, requires about twice as much water as above given for complete solution. Therefore this was of about 10 per cent. strength.

The carbonates tested were as follows: calcite, dolomite, magnesite, siderite, rhodochrosite, smithsonite, aragonite, wither-

ite, strontianite, cerussite, barytocalcite, phosgenite, malachite, azurite, hydrozincite, lansfordite.

These were taken as representative of the common natural carbonates. Each mineral both as lump and powder was tested in cold, warm, and nearly boiling solutions of each reagent. For convenience in recording the results, the following numbers are used in the table to designate the degrees of effervescence.

o. No action.

1. Gas evolved in traces.

2. Gas evolved faintly, but plainly.

3. Gas evolved freely, not strongly.

4. Gas evolved strongly.

5. Gas evolved violently.

The results were, in general, that the powder was acted on more violently than the lump, and the action was stronger as the solution was warmer; but there were exceptions to these rules, which will be noted.

POTASSIUM ACID SULPHATE.

(20 per cent. solution.)

Cold: Nearly half the carbonates were unacted on, or acted on only in traces. *Warm:* All were acted upon, but cerussite, strontianite and phosgenite only faintly, and witherite in traces. In these four cases, the insolubility of the sulphates of the bases present explains the faint action. *Hot:* All were acted upon, the majority strongly, but cerussite and phosgenite yet faintly, and witherite only in traces, as before. With careful observation, this test should positively detect any carbonate with the possible exception of witherite.

The action of this reagent on *calcite, dolomite*, and *magnesite*, is interesting. In lukewarm solutions the powders effervesce as follows: calcite strongly, dolomite freely but not strongly, and magnesite only faintly. This corresponds to their order with hydrochloric acid. But when a *lump* of each is put into *hot* solution, nearly boiling, the order is reversed: Calcite effervesces freely, dolomite strongly, and magnesite violently. The differences are very easily noted, and make this test quite practicable for distinguishing between these minerals. For distinguishing calcite from dolomite, the action of the cold solution on the

powder is also decisive : calcite powder effervesces strongly, at once ; dolomite powder only faintly.

OXALIC ACID.

(10 per cent. solution.)

Cold : About half the carbonates were unacted upon.   *Warm :* All were acted upon, but nearly half only faintly; only two strongly.   *Hot :* All were acted upon, the majority freely, a few only faintly, only one violently.   With ordinary care in observing, this test is satisfactory for all the carbonates tried.

With calcite, dolomite, and magnesite, the effervescence increased in the order given.   In cold solution, calcite was unacted upon either in lump or powder ; dolomite showed traces of gas ; magnesite showed gas evolved plainly.   In hot solution, calcite effervesced freely but not strongly, dolomite strongly, magnesite violently.   The insolubility of calcium oxalate accounts, of course, for this behavior.

CITRIC ACID.

(20 per cent. solution.)

Cold : About half the carbonates were unacted on, or acted on only in traces.   *Warm :* All were acted on, about one-third faintly, one-third freely, and one-third strongly.   *Hot :* All were acted upon, only three (phosgenite, rhodochrosite, and azurite), as low as freely, the rest being strongly to violently affected.

We recommend this reagent as entirely satisfactory, for testing either lump or powder in hot solution.   This reagent also distinguishes clearly calcite from dolomite, for in cold solution calcite effervesces faintly to freely, and dolomite is entirely unacted upon.

TARTARIC ACID.

(20 per cent. solution.)

Cold : Only three carbonates were unacted upon, smithsonite, rhodochrosite, and phosgenite; about half were acted on faintly, the rest freely, one strongly.   *Warm :* All were acted upon, one-third faintly, one-third freely, one-third strongly.   *Hot :* All acted upon, only rhodochrosite and phosgenite as low as *freely*

		Potassium Hydrosulphate. 20 % solution.			Citric Acid. 20 % solution.			Tartaric Acid. 20 % solution.			Oxalic Acid. 10 % sol. with excess of undissolved acid.		
		Cold	Warm	Hot	Cold	Warm	Hot	Cold	Warm	Hot	Cold	Warm	Hot
Calcite	Lump	1 then stops	2	3	1–2	3½	4	2–3	3½	4½	1	2	3
	Powder	4 at once	4	4	2–3	4	5	3–3½	4	4½	2	3	3½
Dolomite	Lump	1 then stops	2	4	0	2	4	1½–1	2	4	1	3	4
	Powder	1 then stops	3	4	3	3	4	1	2	4½	0	3	3
Magnesite	Lump	2	3	5	2–1	2	4	2–1	2	2–1	2–1	3	4
	Powder	1	3	5	0	2	4	1	2	1–2	1–2	3	5
Cerussite	Lump	2–1–0	2	3	1	2	4	1	3	4	1	3	3½
	Powder	1	2	3	3–0	3	4	2–2½	2½	4	2	3	4
Smithsonite	Lump	0	3	3½	0	2	4–3½	0	2	0	3	3	4
	Powder	1	2	4½	0	3	4	2½	3	4½	2	3	4½
Witherite	Lump	0	1	1	3	3	5	3	4	4½	4–1	2	4
	Powder	1	1	1	2	4	4	2½	4	5	4–1	3	4
Strontianite	Lump	3–1	1	3–1	1	3½	4	2½	3	5	3	4	4½
	Powder	3	2	3	2	4	4	3	4	4	3–1	4	4
Barytocalcite	Lump	2½–2	3	3½	2	3	4	2½	4½	5+	3–1	2½	4
	Powder	3	3½	3½	3	4	4	3	4	4	3–1	3	4
Siderite	Lump	1	1	3–2	1	3	4–3½	1	2½	3½–3	0	3	3½–3
	Powder	1	2½	3–2	1½	3	4	2½	3	5+	0	2½	4
Malachite	Lump	3	4	5	3	3	4	2½	3	4	3	3	4
	Powder	3½	4½	4½	1½	4	5	3	4	5	2½	3	4½
Azurite	Lump	3	4	5	0	4	3½	0	3	4	3	3	4
	Powder	3½	4½	4½	3	3½	4½	2	2	4	2	3	3–2
Hydrozincite	Lump	3	4	5	3	3½	5	3	3	3½–3	3–2	3	3–2
	Powder	3½	4½	5	3½	4½	4½	3	2	4	1½	3	2½
Arazonite	Lump	2½–2	2	5–3	3	4½	4½–4	2	4	4½	2–1–0	2	4–3
	Powder	3	3½	4	3	4½	5	3	3½	3–2	1	3½	4½
Phosgenite	Lump	2	2	2½	0	3	4–3	1	3	3–2	1	2½	3–2
	Powder	3	4	5	0	2	5	0	3	3½	2	2½	3–2
Lansfordite	Lump	3	4	5	3½	4½	5	3½	4½	5	3½	4	5
	Powder	4	4½	3–2	4	4½	5	4	4½	5–2	4	4½	5
Rhodochrosite	Lump	0	2	3½–2	1	2	3	0	2½	3½–3	0	2	3½–3
	Powder	1	2	3½	0	2	3½–3	0	2½	3½–3	2	2	3–2

5. Violently. 4. Strongly. 3. Freely, not strong. 2. Faintly, but plainly. 1. In traces. 0. No action.

not strongly, the rest being about half *strongly* and half *violently* affected. This reagent is satisfactory even in warm solution, and still better in hot solution.

Unlike citric acid, it causes dolomite to effervesce in traces even in the cold, while calcite is made to effervesce freely. The distinction is therefore not quite so sharp as with citric acid.

CONCLUSION.

Tartaric acid is the best of the four reagents; citric acid is a close second. Both give satisfactory results in every case tested, using lump or powder in hot solution. Oxalic acid also gives effervescence in every case, in hot solution, and is indeed a practicable reagent, but not so strong as the preceding. Potassium acid sulphate is satisfactory except in the cases of witherite and phosgenite; the rest average low, but the effervescence is sufficient to be easily observed. Bearing these exceptions in mind, it can be used if the other reagents are not at hand.

Some sulphides also effervesce with each of the reagents, giving off hydrogen sulphide, as with hydrochloric acid, and the odor of the gas coming off should therefore be tested, to make sure that the material is not a sulphide.

LEHIGH UNIVERSITY,
January 18, 1900.

REGULATIONS FOR THE TESTING OF THERMOMETERS.[1]

[As Adopted by the Physikalisch-Technische Reichsanstalt, April 1, 1898.]

I. PRELIMINARY REMARKS.

1. Glass thermometers filled with mercury, alcohol, toluene, or any other suitable liquid will be accepted for testing. They will be distinguished as:

a. Standard normal thermometers [*Haupt-Normalthermometer*];

b. Thermometers for scientific purposes (laboratory thermometers);

c. Thermometers for meteorological purposes and for estimating altitudes by boiling-point determinations;

d. Thermometers for technical purposes (factory thermometers);

[1] Translated for the use of the Committee on Standards and for the Journal of the Society by C. E. Linebarger.

e. Thermometers for medical purposes (clinical thermometers);

f. Thermometers for household or domestic use (window-, room-, bath-thermometers, etc.).

The *standard normal thermometers* will be tested only at the Physikalisch-Technische Reichsanstalt, the thermometers for household use only at the testing bureau in Ilmenau.

The Physikalisch-Technische Reichsanstalt is to decide as to the acceptance of thermometers other than the above, unless this is provided for in what follows, although questions as to acceptance may be addressed to the testing bureau at Ilmenau.

Such faults in the construction of all thermometers sent in to be tested, as may give rise to inaccuracies or irregularities in their temperature indications or render their reading too difficult are to be avoided.

2. The testing is done in two stages—the preliminary testing [*Vorprüfung*] and the main testing [*Hauptprüfung*]. The former takes into account all the regulations given in paragraphs 4 to 10, while the latter consists of a regular thermometric examination, beginning with observations, lasting for at least eight days, on the constancy of the indications of the thermometer (by means of determinations of the freezing-point and the like).

The type of the instrument determines whether the further tests shall involve:

a. A determination of the fundamental interval[1] by calibration and comparison with normal thermometers,

b. or only a comparison with normal thermometers in thermostats.

Whenever the divisions on the instrument permit, the amount of the depression of the freezing-point will always be determined and stated in the certificate.

In the testing of a maximum or minimum thermometer (for medical, meteorological, or other purposes), besides the comparison stated in *b*, experiments will be made to ascertain whether the instrument works properly. The errors in both series of tests for such thermometers should not differ when the divisions are

[1] [The fundamental interval is the scale interval between the normal boiling-point and the normal freezing-point, the latter being taken at the lowest position observed.]

$\frac{1}{10}°$ or $\frac{1}{4}°$ by more than 0.08° C.

$\frac{1}{4}°$ " $\frac{1}{2}°$ " " " 0.2° C.

The differences in the readings of maximum thermometers *at* a given temperature and *after* cooling, should not in the case of clinical thermometers amount to more than 0.15° C. In the case of maximum thermometers of other kinds the allowable differences are to be estimated from the length of the mercury column.

Tests will also be made to ascertain whether the device for recording the maximum temperature offers too great a resistance when the mercury is shaken down.

3. The fundamental temperature scale shall be that of the hydrogen thermometer as adopted for the international system of weights and measures according to a resolution of the *Bureau international des Poids et Mesures*, on October 15, 1887.

II. GENERAL REGULATIONS.

4. The glass used in the construction of the thermometers should have the least possible thermal hysteresis [*thermische Nachwirkung*]. When glass is employed whose hysteresis is not sufficiently known or which is found to be too great, the thermometers must be allowed to stand from one to four months, the sender being notified of such action.

Thermometers which are to be tested at temperatures above 100° C., as well as all finer thermometers such as listed in paragraph 1, under *a*, *b*, and *c*, must be subjected to an artificial aging process before they are sent in. This consists in heating them for ten to thirty hours, according to the temperatures they are intended to indicate, to the highest temperature they register, and then cooling them slowly. Notice must therefore be given when the thermometers are sent in as to whether this heating has been done or not.

Thermometers reading to 550° C. should be made of Jena borosilicate glass 59$^{\text{III}}$ or some similar difficultly fusible glass; those reading to 420° may also be made of Jena normal thermometer glass 16I$_{\text{I}}$I (with red-violet stripe) or of Greiner and Friedrichs' resistance glass (with blue stripe).

5. The capillary tube must be clean and of uniform bore. Thermometers of the types *a*, *b*, *c*, and *d*, in paragraph 1, are to have a pear-shaped bulb blown in their upper end. Bulbs blown

in the capillary tube itself must be there for a purpose and must not occasion a narrowing of the adjacent parts of the tube (unless, indeed, such constrictions are meant to serve a special object), which might cause a separation of the mercury during transportation or use. The upper end of the capillary must be in plain sight and not covered by the cap.

6. The mercury must be pure and dry and threads of it must not break off when it is retreating into the bulb. The mercury column should not separate at any place when the thermometer is inverted without jarring. Exceptions to this may be allowed in the case of thermometers with very long stems or large bores or with especially large bulbs.

Any other liquids used to fill the thermometers must be of such a nature that, when the column of liquid is retreating into the bulb, visible drops do not remain behind, and the coloring-matter that may be employed does not separate out.

The use of liquids with too low boiling-points is to be avoided as there is danger of their distilling over into the end of the capillary.

Thermometers designed to measure temperatures over 280° C. must be filled above the mercury with some dry gas (nitrogen, carbon dioxide, and the like) under proper pressure.

7. The scale-divisions must be durable and without any easily apparent errors. In the case of enclosed thermometers[1] [*Einschluss-thermometer*] the scale-divisions must be as close as possible to the capillary so as to insure definite and accurate readings at all positions.

The length of the shortest scale-division on a stem thermometer[2] [*Stab-thermometer*] should in general be at least $\frac{1}{6}$ of the circumference of the tube.

The nature of the division must be designated by the words *hunderttheilig* ["hundred-degreed"], Celsius, etc., and the divisions must be plainly numbered. Division marks must not be placed on widened parts of the capillary.

Division marks should not extend *unnecessarily far* above the temperature interval to be employed. Still a few divisions must

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[1] Enclosed thermometers are such as have a small capillary tube lying against a scale and all enclosed in a larger tube.

[2] In stem thermometers the scale-divisions are cut or etched directly on the capillary tube.

always be marked above the highest and below the lowest of the parts of the scale to be tested.

Thermometers with Réaumur scales will not be tested. Exception to this rule will be made until the end of 1900 in the case of thermometers for technical use (*cf.* paragraph 1, *d*).

8. The scales of enclosed thermometers must be fastened securely and firmly, but must permit of free expansion without bending in one direction with reference to the enclosing tube. Thermometers with paper scales will be tested only up to 60° C.

The position of the scales with reference to the capillary or the enclosing tube is to be controlled by means of a mark which, when possible, will be placed on the *right-hand* side of the thermometer and is in no wise to interfere with the reading at that point.

The enclosing tube of enclosed thermometers should, unless exceptions be allowed according to the special regulations (paragraphs 11 to 16), be fused together at the upper end or be provided with a second mark in the vicinity of the end of the scale.

9. Only thermometers of the types *d* and *f* (technical and household thermometers) may have detachable scales. The tubes of such thermometers must be firmly fastened, must lie close to the scale, and must bear marks to control their position. The fastenings must be so arranged that they may be removed for testing and marking.

Thermometers with detachable scales will have both tube and scale marked (*cf.* paragraph 17).

10. Thermometers may bear the maker's number, trade-mark, etc., but nonsensical marks and such as are contrary to the results of the testing will not be permitted.

Maximum and minimum thermometers must be specially marked as such.

There must be on every thermometer sufficient room to place the official mark or stencil (*cf.* paragraph 17), and any other needed marks (*cf.* paragraph 18).

III. SPECIAL REGULATIONS.

In what follows are given the requirements for testing and the allowable limits of error for the different types of thermometers listed in paragraph 1.

11. *Standard normal thermometers* must be mercury-in-glass thermometers, bearing the points o and 100 on their scale and must permit of direct calibration. They will be tested exclusively by the Physikalisch-Technische Reichsanstalt.

The divisions of these thermometers must be uniform and made without regard to the errors of calibration. The errors of division should not exceed $\frac{1}{20}$, and the width of a mark $\frac{1}{10}$, of the smallest interval.

The capillary tube must have a pear-shaped widening at its upper end and must be free from air. The examination of these thermometers will be made between the temperature-limits,—30° to + 100°C. and for every 10° at least.

The limits of error are:

1. For the fundamental interval, 0.10° C.;

2. For the error of calibration as the difference of the greatest deviations, 0.25° C.;

3. The depression of the freezing-point after a half-hour's heating to 100° C. and subsequent imbedding of the thermometer in ice for five minutes should not amount to more than 0.10°C.

The certificate will give in 0.001° the corrections for calibration, fundamental interval, freezing-point, and reduction to the gas-thermometer and also the aggregate error rounded off to 0.01.°

12. *Laboratory thermometers* are such as are employed in scientific and technical investigations in the laboratory for the measurement of temperatures from —80° to + 550° C.[1]

The limits of error are:

For the temperature interval		When the scale is divided into	
		integral degrees or multiples thereof.	fractions of a degree.
from — 80° to — 30°		2° C.	1.° C.
" — 30° " 0°		1	0.5
" 0° " 100°		0.5	0.25
" 100° " 200°		1	0.5
" 200° " 300°		2	1
" 300° " 400°		3	2
" 400° " 550°		5	4

[1] Until further notice the scale of the air thermometer shall be standard for temperatures over 100° C., as the international agreement (*cf.* paragraph 3) has reference only to the interval between 0° and 100°, the comparison with the hydrogen thermometer having not yet been finished.

Tests are made when the divisions are in

$\frac{1}{10}$° C. for at least every 10°,

$\frac{1}{5}$° C. for at least every 15°,

$\frac{1}{4}$ or $\frac{1}{5}$° C. for at least every 20°, when the length of 10° is more than 40 mm.

$\frac{1}{2}$ or $\frac{1}{5}$° C. for at least every 25°, when the length of 10° is more than 20 mm. and less than 40 mm.

$\frac{1}{4}$ or $\frac{1}{5}$° C. for at least every 50°, when the length of 10° is more than 8 mm. and less than 20 mm.

$\frac{1}{4}$ or $\frac{1}{5}$° C. for at least every 100°, when the length of 10° is less than 8 mm.

13. (1) By *meteorological thermometers* are meant those used in finding the temperature of the air, of natural waters, of the earth's crust, of the sun's radiation, of the dew-point, etc. The scale may embrace any interval between —70° and + 100° C.

Tests are made

When the divisions are in		Limits of error.
$\frac{1}{4}$ or $\frac{1}{10}$° C.	For every 10°, at least.	Same as given in
$\frac{1}{4}$ " $\frac{1}{5}$° "	" " 20°, " "	paragraph 12.

(2) Thermometers for the measurement of altitudes by boiling-point determinations may be divided either in centigrade degrees or in millimeters of tension of water-vapor under various pressures and may embrace the interval + 70 to 102° C.; they may also have an auxiliary scale near the zero-point. To prevent as much as possible any changes in these thermometers when used for some time on scientific expeditions, they should be subjected to an artificial aging process (*cf.* paragraph 4) before they are sent in.

Tests will be made for every 4°, at least, or in case a millimeter scale is used, for every 50 mm. The errors should not exceed 0.1° C. or 3 mm. respectively. If an auxiliary scale be attached at 0°, the depression of the freezing-point will be determined after the thermometer has been heated for half an hour to 100°; it should not amount to more than 0.1° C. If, however, an auxiliary scale is not attached, the depression of one of the lowest points of the scale will be determined.

14. The testing of *thermometers for technical purposes*, because of the multiplicity of their forms and the unusually large

dimensions of some of them, can be undertaken only as the facilities at hand permit.

The limits of error for these thermometers may be double those given in paragraph 12.

Thermometers made of glass free from thermal hysteresis up to 100° C. whose errors are all less than 0.05° C. are termed free from error. The number of points on the scale that will be tested is fixed according to the regulations given in the same paragraph, unless the thermometers be uncommonly long.

In the case of long technical thermometers the capillary connecting the bulb and scale must be so fine that the indications of the thermometer will not be appreciably affected by the temperature of the neck, due regard being given to the degree of accuracy required of such thermometers. If tests are to be made at higher temperatures on factory thermometers having long necks whose volume cannot otherwise be reliably ascertained, they must be sent in before they are filled under pressure so that the volume of the connecting capillary can be determined.

15. *Has to do with the limits of error, etc., of clinical thermometers.*

16. *Treats of limits of error, etc., of household thermometers.*

IV. CERTIFICATES, CHARGES AND TIME REQUIRED FOR TESTING.

17. Thermometers with which certificates are given will be marked to show that they have been tested by the Physikalisch-Technische Reichsanstalt with the Imperial Eagle (*Reichsadler*) and P T R, and to show that the testing has been done at Ilmenau, with the Imperial Eagle and G S.

They are also marked with a number, with which *all* thermometers with the exception of such clinical thermometers as have been found unsuitable for testing are provided.

In addition, the year is given for all thermometers listed in paragraph 1, under *a, b, c,* and *d.*

Besides the thermometric errors, the certificate contains indications, when necessary, as to the kind and application of the thermometer in question.

The rounding-off of the thermometric errors found by the tests depends upon the nature of the scale and the results of the

testing, except where a special procedure is prescribed for the individual classes of thermometers in the foregoing regulations.

As a rule the errors observed are given for the thermometers in a vertical position and with the *whole* of the liquid column immersed in the bath.

If the use of the thermometer requires the liquid column to emerge from the bath whose temperature is to be measured, information must be given when the thermometer is sent in, as to how deep the thermometer must dip into the bath and what the temperature of the emergent column may be assumed to be.

18. *Charges for testing.*

19. Thermometers will be tested in the order of their receipt as shown by the post-mark; the preliminary tests will be made at once upon the receipt of the thermometer. The tests will be finished in from three to four weeks according to their nature and the amount of work on hand.

APPENDIX.

20. *Recommendations as to the packing and sending of thermometers.*

A NEW SYNTHESIS IN THE QUINAZOLINE GROUP.[1]

(PRELIMINARY ANNOUNCEMENT.)

BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF.

IN the course of some researches carried on in this laboratory by J. A. Mathews on "The Action of Nitriles upon Aromatic Acids,"[2] it was discovered that when anthranilic acid and acetonitrile were heated together in a sealed tube for five hours at 220°–230° C., instead of obtaining orthoamidobenzonitrile as expected, there resulted a crystalline product melting at 232°. This body was boiled with strong hydrochloric acid, and the solution on cooling deposited long needles which sublimed at about 280° without melting. Not enough of the substance, however, was secured for an analysis, and hence its nature could not be determined.

[1] Read before the New York Section, February 9, 1900.
[2] This Journal, 20, 654.

The writers have continued this investigation, and, by varying the conditions slightly, have readily obtained very fair yields of this substance and identified it as the 2-methyl-4-ketodihydroquinazoline first described by Weddige[1] and later obtained by Bischler and Burkart,[2] Bischler and Lang,[3] and Niementowski[4] The needles obtained by Mathews by the action of hydrochloric acid were, of course, only the HCl salt.

The reaction by which the quinazoline compound is produced from anthranilic acid and acetonitrile is easily explained when it is remembered that, under conditions of heat and pressure, a nitrile tends to combine with an organic acid to form a secondary amide, as shown first by Gautier,[5] and later, in this laboratory, confirmed by the work of Colby and Dodge.[6] The reaction, therefore, probably takes the following course :
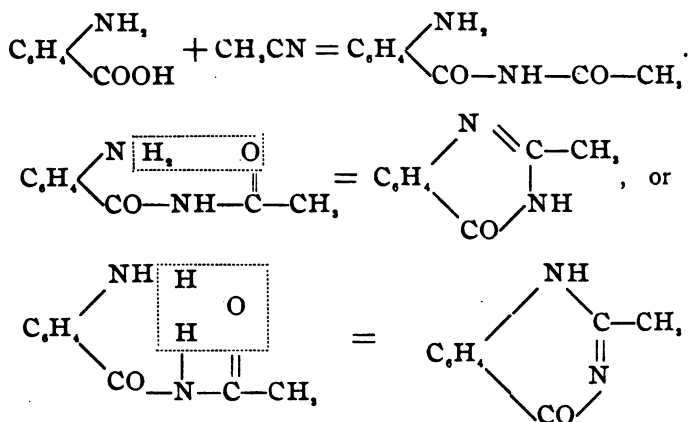
As early as 1860, Griess and Leibius[7] studied the action of cyanogen gas upon the amidobenzoic acids, and in 1869, Griess[8] obtained condensation products by passing cyanogen gas into aqueous and alcoholic solutions of anthranilic acid. The condensation products, however, were due entirely to a preliminary

[1] J. prakt. Chem. (2), 31, 124.
[2] Ber. d. chem. Ges., 26, 1350.
[3] Ibid., 28, 282.
[4] J. prakt. Chem. (2), 51, 564; and Ber. d. chem. Ges., 29, 1360.
[5] Ztschr. Chem. (1869), 127.
[6] Am. Chem. J., 13, 1.
[7] Ann. Chem. (Liebig), 113, 332.
[8] Ber. d. chem. Ges., 2, 415.

amidine union between the cyanogen and amido groups, which in our synthesis is very improbable, both on account of the less acid character of the nitriles employed and also because Bernthsen has shown[1] that benzonitrile and aniline have no appreciable action upon each other even at 360° C. The products obtained would also be far different from those which we have separated.

The reaction of Niementowski,[2] by which he obtains quinazoline derivatives through the interaction of an amide upon anthranilic acid, appears to be a simultaneous condensation between the amido and carbonyl groups of the amide and the carboxyl and amido groups of the anthranilic acid, and is, possibly, in its internal mechanism, somewhat related to the nitrile synthesis under discussion. Niementowski found, however, that while the yield with formamide and acetamide was excellent, as the molecular weight of the amide increased it became less and less satisfactory, the higher temperature required producing more and more decomposition, and consequently more by-products, while with benzamide the condensation failed entirely and no quinazoline body could be obtained.

With our synthesis, on the other hand, using nitriles instead of amides, the reaction proceeds just as smoothly with aromatic nitriles as with aliphatic ; the contents of the tubes are invariably crystalline and free from by-products (except a small amount of carbonaceous material), and by treating with boneblack and crystallizing twice from alcohol, the quinazoline body is obtained pure. We have thus prepared with the greatest ease the following derivatives of the 4-ketodihydroquinazoline, together with many of their salts :

2-Methyl.—Identical with that described by Weddige.[3]

2-Ethyl.—Already described by Bischler and Lang,[4] and by Niementowski.[5]

2-Phenyl.—Isomeric with, but not the same as the phenyl derivative of Körner,[6] the isomerism probably being due to a different position of the double bond in the miazine nucleus (at (1), instead of (2) ?).

[1] *Ann. Chem.* (Liebig), **184**, 349, foot-note.
[2] *J. prakt. Chem.* (2), **51**, 564.
[3] *Ibid.* (2), **31**, 124.
[4] *Ber. d. chem. Ges.*, **28**, 284.
[5] *J. prakt. Chem.* (2), **51**, 568.
[6] *Ibid.* (2), **36**, 155.

2-Benzyl.—New.

2-Paratolyl.—New.

The description of these bodies and their derivatives, together with many others upon which we are now at work, will be presented later. So much work has been and is being done upon quinazolines that we have deemed it wise, before entering upon the very extensive field which this new synthesis opens up, to present this preliminary notice, that we may be left free to continue our work without fear of molestation.

We should like, therefore, to reserve for the Organic Laboratory of Columbia University, the study of the action of cyanogen compounds upon organic acids, as we shall endeavor to extend this research to bodies of the aliphatic series (in the hope of obtaining oxypyrimidine compounds), as well as to other classes of compounds. We are also investigating the action of nitriles upon other ortho-substituted acids, etc., and upon closely related bodies.

When one considers the ease with which the nitriles can be obtained, especially in the aromatic series, and the fact that all the nitriles used so far, both aliphatic and aromatic, react with the same facility, it does not seem too much to say that this new process appears likely to prove the most widely applicable and most important synthesis for quinazoline compounds yet discovered.

ORGANIC LABORATORY, HAVEMEYER HALL,
    COLUMBIA UNIVERSITY, February 1, 1900.

A COMPARISON OF SOME FORMALDEHYDE TESTS.[1]

BY B. M. PILHASHY.
Received February 5, 1900.

HAVING had occasion to make some qualitative tests to show the presence of formaldehyde, I reviewed the recent chemistry for the detection of formaldehyde. In some instances the reaction given for formaldehyde proved to be true for other aldehydes also and apparently for distilled water. In some cases the delicacy of the reaction given for a particular reagent was not true for the stated dilution, while in others the reaction was clear and not to be doubted. The following summary of

[1] Read before the Cincinnati Section, November 15, 1899.

various reactions for the more common aldehydes may prove useful to others, who may have occasion to work in the same line.

(*a*) *Schiff's Reagent.*—Most aldehydes in dilute solutions give a violet coloration with this reagent. (Fuchsin decolorized by sulphurous acid.) This can also be obtained by mere exposure of the reagent to the air or by warming the suspected liquid with the reagent even in the absence of an aldehyde.[1]

(*b*) *Phenol and Sulphuric Acid.*—Most aldehydes give with very dilute phenol and sulphuric acid added to form a layer beneath, a scarlet ring changing to dark red on heating.[2]

(*c*) *Diazobenzenesulphonic .Acid.*—Most aldehydes with this reagent in the presence of free alkali and sodium amalgam give an intense violet color at once or within twenty minutes. The colors are destroyed by exposure or by acid.[3]

(*d*) *Nessler's Solution.*—Acetaldehyde as well as formaldehyde gives a precipitate with Nessler's solution. They also give a precipitate with anilin.[4]

(*e*) *Dimethylanilin and Sulphuric Acid.*—Trillat gives the following reaction for formaldehyde alone. To a dilute solution a few drops of sulphuric acid and also of dimethylanilin are added. The mixture is heated for half an hour on a water-bath, made alkaline and further heated to drive off the excess of dimethylanilin which can be detected by its odor. The liquid is then filtered and the paper moistened with acetic acid. If formaldehyde is present, a blue coloration results when lead dioxide is then sprinkled on the paper.[5]

The following experiments tend to show that this reaction is due to dimethylanilin present.

Experiment 1.—If a piece of filter-paper be moistened with a very dilute solution of dimethylanilin in water it will give the blue color reaction with lead dioxide and acetic acid.

Experiment 2.—Twenty cc. distilled water, 2 drops of sulphuric acid, and 1 drop of dimethylanilin were mixed, forming

1 Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 217.
2 *Ibid.*
3 *Ibid.*
4 *Ibid.*
5 *Ibid.*, p. 220.

a very dilute acid solution. This was heated one-half hour, during which time 100 cc. distilled water were added at intervals to replace that evaporated. After heating a while a strip of filter-paper dipped into this solution gave a yellow color with lead dioxide and acetic acid. Another strip dipped into the solution and made alkaline with ammonium hydroxide or sodium carbonate solution gave a slight blue after ten minutes. At the end of the heating these reactions could not be again obtained pointing to a probable volatilization of the salt formed.

Experiment 3.—Instead of the distilled water in Experiment 2, 20 cc. formaldehyde solution (1 : 1000) were used. After heating for one-half hour a strip of filter-paper moistened with the solution gave the yellow color observed in Experiment 2, with the lead peroxide and acetic acid and the blue color with the same reagents after making alkaline. The outside of the dish was coated with a yellow salt which was washed into a dish, made alkaline and filtered. The filter-paper gave the before-mentioned blue reaction.

Experiment 4.—A few drops of dimethylanilin were dissolved in water with the aid of a few drops of sulphuric acid. A strip of paper moistened with it gave the yellow reaction with lead peroxide and acetic acid. The solution was neutralized and filtered. The filter-paper as well as a strip moistened with the solution gave the blue coloration as above.

Experiment 5.—Twenty cc. formaldehyde solution (1 : 1000), 2 drops of sulphuric acid, and 1 drop of dimethylanilin were heated for one-half hour, made alkaline with sodium hydroxide solution and then heated for one hour longer to drive off any free dimethylanilin in excess. There was no odor to the solution which was filtered. The filter-paper gave no blue coloration with lead peroxide and acetic acid.

SUMMARY.

From the foregoing experiments it seems that Trillat's test does not show the presence of formaldehyde, but of dimethylanilin or its salts when not completely volatilized.

(*f*) *Lebbin's Test*.[1]—This is said to be delicate enough to detect 1 part formaldehyde in 10,000,000 of water. In my experience 1 in 200,000 seems to be the limit.

(*g*) *Morphin hydrochloride*[2] with sulphuric acid is not to be considered sensitive enough for formaldehyde in a more than 1 : 1000 solution, a purple ring being obtained.

(*h*) *Phenylhydrazin hydrochloride*[3] seems to be the best reagent for formaldehyde. The solution of 1 gram of phenylhydrazin hydrochloride with 1.5 grams sodium acetate in 10 cc. water is used. To 1 cc. of the liquid 2 drops of the reagent and 2 drops of sulphuric acid are added producing a green coloration. In as dilute a solution as 1 : 10,000 or 1 : 100,000, 3 cc. of the liquid with 4 drops of the reagent and 4 drops of sulphuric acid heated for half a minute bring out the color. For 1 : 250,000, 3 cc. of the liquid with 5 drops of the reagent and 5 drops of sulphuric acid heated for about a minute, give a very light tinge of green after three minutes, a decided tint after ten minutes.

(*i*) Rimini[4] uses *phenylhydrazin hydrochloride with sodium nitro-prusside and concentrated sodium hydroxide*, a blue coloration resulting. One part in 1,000 and 1 in 10,000 give an intense blue when 1 cc. of the solution is mixed with 2 drops each of phenylhydrazin hydrochloride solution and of sodium nitro-prusside solution, 1 cc. of caustic soda solution being then added. One in 100,000 gives a deep blue, and one in 1,000,000 gives a light blue. These blues change quickly to green, yellow, light brown, and red. A peculiarity is the rise of the red color to the top leaving a yellow layer below. Both layers are clear solutions. If the same amount of reagent as given above be added to dilutions greater than 1 in 1,000,000, about the same shade of blue is obtained for them,—hence the limit seems to be 1 in 1,000,000.

[1] Allen's "Commercial Organic Analysis," Vol. I, 3rd edition, p. 220.
[2] *J. Soc. Chem. Ind.*, Abst., p. 955 (1898).
[3] *Ibid.*, p. 954.
[4] *Ibid.*, p. 697.

SOME NEW TELLURIUM COMPOUNDS.

BY VICTOR LENHER.

I N many points tellurium resembles selenium in its derivatives, the oxides are not unlike in their behavior, and the tellurites and tellurates are very similar to the corresponding selenites and selenates.

Tellurium, owing to its high atomic weight, shows greater stability in its higher halogen derivatives than the preceding members of the group to which it belongs. Two series of halides are known, corresponding to TeX_2 and TeX_4. The tetrahalides are those most commonly met with and seem to be the type which tellurium tends to follow with the halogens. With selenium, on the contrary, we find the lower halides are the more stable. Heat transforms the tetra- into the monohalides with corresponding loss of halogen.

As in the case of the other natural groups of elements, the basic property is found to increase with the rise in atomic weight, so here also we find the same tendency in the higher members to be more basic than the lower ones. Sulphur is a decidedly acid element; in selenium this property is decidedly weaker, while with tellurium we actually find such salts as the tartrate, basic sulphate, and basic nitrate, which are not known in the case of a true non-metal. In appearance, tellurium resembles a metal, while sulphur and selenium, in the elementary condition, certainly do not appear metallic.

As a result of this increase in basic properties, we should expect to find that tellurium forms better defined double halides than selenium. This is actually the case. Only the double bromides of selenium are known. Attempts to prepare double chlorides thus far have proved unsuccessful, and likewise the formation of double bromides of selenium is restricted within certain limits.

It has been shown by the author[1] that selenium tetrabromide can unite with the hydrobromides of the organic amines to form

[1] This Journal, 20, 572.

well-defined double salts in which the amine plays the rôle of ammonia in the compound $(NH_4)_2SeBr_6$. Norris[1] has also prepared a number of the double halides of selenium.

When tellurium replaces selenium in the double halides, we obtain more clearly defined compounds than is the case with the latter. In fact, while selenium tetrabromide unites with only the hydrobromides of the fatty amines and with the hydrobromides of pyridine and piperidine, no compound could be prepared with any of the true aromatic amines or with quinoline ; neither has it been possible to prepare an aromatic or aliphatic amine salt in which selenium tetrachloride replaces the tetrabromide.

Both tellurium tetrabromide and tetrachloride form a series of beautiful salts with the aliphatic amines, and both of the halides also unite with the aromatic amines to form well-defined derivatives. In the series of salts which has been prepared, it is somewhat striking to notice that all the bromides are red while the chlorides are invariably yellow. Wheeler[2] has shown that the double chlorides of tellurium with potassium, rubidium, and cesium are yellow while the corresponding bromides are red.

To prepare the salts it is only necessary to add a solution of tellurium dioxide in hydrochloric or hydrobromic acid to the amine salt dissolved in the corresponding acid ; a precipitate of the double salt generally forms immediately, and this precipitate, when recrystallized from dilute acid, gives crystals of the salt in a purified condition.

All the double salts are decomposed by pure water with the formation of hydrated TeO_2, but are soluble in dilute acids and in alcohol.

Method of Analysis.—Great difficulty was at first experienced in making an analysis of these compounds, owing to the complications which invariably ensued. The method which was finally adopted consisted in dissolving a weighed quantity of the salt in a dilute solution of tartaric acid, adding to this a measured excess of standard silver nitrate and a few drops of ferric alum. The solution was then treated with a standard solution of ammonium thiocyanate. The object of the tartaric acid was

1 *Am. Chem. J.*, 20, 490.
2 *Ztschr. anorg. Chem.*, 3, 428.

to hold in solution the tellurium dioxide, which otherwise would be precipitated by the water, and to prevent the formation of a precipitate of silver tellurite which would interfere with the titration. When a sufficient quantity of tartaric acid is present to hold tellurium dioxide in solution and prevent its action on the silver, the method proves very accurate. The silver nitrate solution was made up of such strength that 1 cc. = 0.007969 gram bromine or 0.003533 gram chlorine.

Methylamine Bromotellurate, $(CH_3NH_3)_2TeBr_6$.—To a solution of methylamine in hydrobromic acid, a hydrobromic acid solution of TeO_2 was added, when a red precipitate immediately formed. This was collected on a filter and the salt purified by recrystallization from dilute hydrobromic acid.

0.3023 gram salt required 27.1 cc. silver nitrate solution.

	Calculated for $(CH_3NH_3)_2TeBr_6$.	Found.
Br	71.50	71.44

The crystals are of a red color and are regular octahedrons, having a high index of refraction.

Methylamine Chlorotellurate, $(CH_3NH_3)_2TeCl_6$.—This substance was prepared in a manner similar to the preceding; that is, a hydrochloric acid solution of tellurium dioxide was added to a solution of the amine in hydrochloric acid and the product recrystallized from dilute hydrochloric acid.

0.3029 gram salt required 44.9 cc. silver nitrate solution.

	Calculated for $(CH_3NH_3)_2TeCl_6$.	Found.
Cl	52.67	52.37

The crystals appear as yellow hexagonal plates, with a micaceous cleavage. The index of refraction is low, and in polarized light a low order of colors is shown.

Ethylamine Bromotellurate, $(C_2H_6NH_3)_2TeBr_6$.—Exactly the same procedure was adopted in the preparation of this salt as with the methylamine derivative.

0.3056 gram salt required 26.3 cc. silver nitrate solution.

	Calculated for $(C_2H_6NH_3)_2TeBr_6$.	Found.
Br	68.63	68.58

The crystals are red hexagonal plates which show a strong

basal cleavage.   In polarized light the colors are of a low order, and the refractive index is fairly high.

Ethylamine   Chlorotellurate, $(C_2H_5NH_3)_2TeCl_6$.—This   salt forms yellow hexagonal plates showing a strong cleavage, and in polarized light showing a low order of colors.

0.3034 gram salt required 42.1 cc. silver nitrate solution.

	Calculated for $(C_2H_5NH_3)_2TeCl_6$.	Found.
Cl......................	49.24	49.02

Trimethylamine   Bromotellurate, $[(CH_3)_3NH]_2TeCl_6$.—This salt is the most strongly crystalline of all the compounds prepared.   It forms red orthorhombic crystals which have a fairly high index of refraction.   The crystals show a low order of colors in polarized light, but in convergent light a biaxial figure is readily seen.

0.3029 gram salt required 24.9 cc. silver nitrate solution.

	Calculated for $[(CH_3)_3NH]_2TeBr_6$.	Found.
Br......................	65.98	65.51

Aniline Bromotellurate, $(C_6H_5NH_3)_2TeBr_6$.—The action of the bromide of tellurium on aniline hydrobromide is quite unlike that of selenium tetrabromide.   In the case of selenium, no compound seems to be formed, the aniline actually reducing the bromide of selenium even in acid solution.

When a solution of tellurium dioxide in hydrobromic acid is added to aniline hydrobromide, a red precipitate forms, which can be purified by recrystallization from dilute hydrobromic acid.   The salt then appears as red monoclinic tablets which act strongly on polarized light.

0.3053 gram salt required 23.3 cc. silver nitrate solution. ·

	Calculated for $(C_6H_5NH_3)_2TeBr_6$.	Found.
Br......................	60.34	60.82

Aniline Chlorotellurate, $(C_6H_5NH_3)_2TeCl_6$.—While selenium tetrabromide does not enter into combination with aniline hydrobromide, tellurium tetrabromide as has been seen, readily forms a double salt.   The formation of double chlorides with selenium remains yet to be shown, while here we have the first example of the union of tellurium tetrachloride with the salt of an aro-

matic amine. This salt, which was prepared in a manner simi-
lar to the preceding is, like all of the chlorides, yellow in color.
The crystals of the salt were too small to determine their form,
but they are active to polarized light. The salt is very light
and feathery.

0.3017 gram salt required 34.2 cc. silver nitrate solution.

	Calculated for $(C_5H_5NH_2)_2TeCl_6$.	Found.
Cl	40.25	40.04

Pyridine Bromotellurate, $(C_5H_5NH)_2TeBr_6$.—This compound
forms fine red crystals, not large enough to determine the crys-
tallographic system of the salt, but it was found to be active to
polarized light.

0.3041 gram salt required 24.1 cc. silver nitrate solution.

	Calculated for $(C_5H_5NH)_2TeBr_6$.	Found.
Br...................	62.55	63.15

Pyridine Chlorotellurate, $(C_5H_5NH)_2TeCl_6$.—This salt forms
yellow isometric crystals having a low index of refraction. The
crystals were very small.

0.3012 gram salt required 36.2 cc. silver nitrate solution.

	Calculated for. $(C_5H_5NH)_2TeCl_6$.	Found.
Cl	42.54	42.46

Quinoline Bromotellurate, $(C_9H_7NH)_2TeBr_6$.—Very small red
crystals of the salt were obtained, which were found to act on
polarized light.

0.3026 gram salt required 21.00 cc. silver nitrate solution.

	Calculated for $(C_9H_7NH)_2TeBr_6$.	Found.
Br....................	55.32	55.30 ·

Quinoline Chlorotellurate, $(C_9H_7NH)_2TeCl_6$.—The crystals of
this salt were also very small and were active to polarized light.

0.3051 gram salt required 30.6 cc. silver nitrate solution.

	Calculated for $(C_9H_7NH)_2TeCl_6$.	Found.
Cl	35.44	35.43

It thus appears that both the tetrachloride and tetrabromide
of tellurium readily form double salts with the salts of both the
fatty and the aromatic amines. The salts crystallize well,

and their color seems to be dependent on the halogen content, the bromides being invariably red, and the chlorides yellow.

A solution of tellurium dioxide in halogen acids gives a precipitate with nearly all of the alkaloids, probably forming salts similar to those above described. The alkaloid derivatives are now being studied in this laboratory.

THE ACTION OF α-ACYLATED PHENYLHYDRAZINES ON THE CHLORINE DERIVATIVES OF QUINONES.

(PRELIMINARY REPORT.)

BY WILLIAM McPHERSON AND ROBERT FISCHER.

THE investigations of Zincke[1] on the interaction of phenyl-hydrazine and the quinones led to the general result that α-naphthoquinone, β-naphthoquinone, and phenanthraquinone condense in a normal manner with phenylhydrazine, but that under similar conditions, all of the quinones of the benzene series give hydroquinones, the reaction being attended with gas evolution. Many subsequent efforts have been made to effect a normal condensation between benzoquinone and phenylhydrazine, since this reaction would help to solve the problem of the constitution of the oxyazo-bodies. Although this has not as yet been accomplished, it has been shown by one of us[2] that the unsymmetrical acylated phenylhydrazines, e. g., $C_6H_5.N.C_7H_5O.NH_2$, condense with benzoquinone in a normal manner forming a hydrazone derivative in accordance with the following equation :

$$C_6H_4\!\!\stackrel{O}{\underset{O}{\diagup\diagdown}} + H_2N.C_7H_5O.N.C_6H_5 = C_6H_4\!\!\stackrel{O}{\underset{N-C_7H_5O.N.C_6H_5}{\diagup\diagdown}}$$
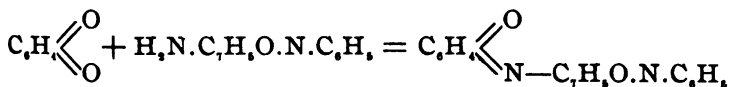
This reaction has recently been extended to the chlorine derivatives of quinone. It has been found, however, that while the α-acylphenylhydrazines react with these readily, the compounds formed are not hydrazones but *hydrazino* derivatives, possessing a structure similar to the so-called anilidoquinones, formed by the interaction of quinones and aniline under certain conditions. With trichlorbenzoquinone the following reaction

[1] *Ber. d. chem. Ges.*, **16**, 1563.

[2] *Ibid.*, **28**, 2414 ; *Am. Chem. J.*, **22**, 364.

takes place, the two hydrogen atoms being removed by the oxi-
dizing action of a second molecule of the quinone.

$$\text{(tetrachloroquinone)} + \boxed{H}NH.C_6H_5.O.N.C_6H_5 =$$

$$\text{(trichloroquinone)}\ C-NH-C_6H_5.O.N.C_6H_5 + H.$$
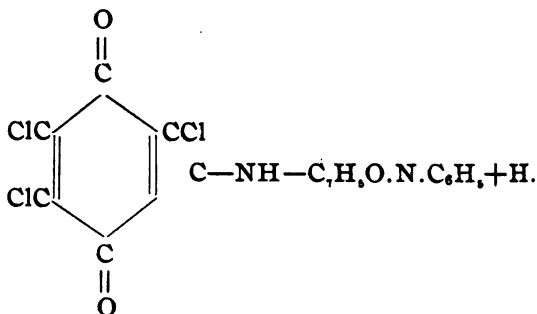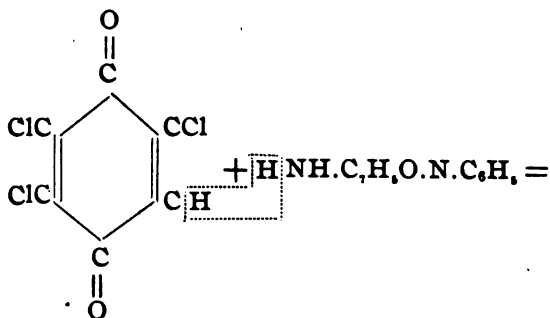
This reaction is analogous to the interaction of trichlorqui-
none and aniline, investigated by Niemeyer,[1] the point of attack
being the hydrogen of the quinone in preference to the chlorine.

Tetrachlorquinone gives with α-benzoyl phenylhydrazine the
same product as trichlorquinone, hydrochloric acid being evolved.

It is quite probable that under different conditions, hydrazone
derivatives of the chlorquinones may be obtained. This subject
is now under investigation in this laboratory. The interaction
of the quinones and the unsymmetrical naphthylhydrazine deriv-
atives is also being studied with the hope of isolating both the
true oxyazo-bodies and their isomeric quinonehydrazones and
thus definitely deciding the constitution of the so-called free
oxyazo-bodies.

[1] *Ann. Chem.* (Liebig), **228**, 322.

EXPERIMENTAL PART.

Action of α-Benzoyl Phenylhydrazine on Trichlorbenzoquinone.—
α-Benzoyl phenylhydrazino trichlorquinone,

$$O = C \underset{CCl = C - NH - C_7H_5ON.C_6H_5.}{\overset{CCl = CCl}{\Big\langle \quad \Big\rangle}} C = O$$
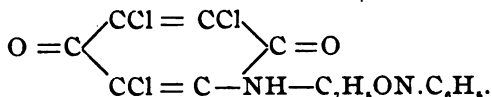
The hydrazine was prepared according to Widman's excellent method,[1] for the preparation of unsymmetrical hydrazines.   Some slight changes in the process were found advantageous.   In the case of α-benzoyl-β-acetylphenylhydrazine the following method easily gives the pure solid product, in place of the difficultly solidifying oil which Widman first obtained.   To 10 grams of pure β-acetylphenylhydrazine were added 70 grams of benzene and 9.4 grams of benzoyl chloride.   The flask was connected with a return condenser and its contents heated to boiling.   The hydrazine slowly dissolved with evolution of hydrochloric acid. After heating for a few minutes the α-benzoyl-β-acetylphenyl-hydrazine began to separate on the sides of the flask owing to the slight solubility of the body in benzene.   After heating for one hour, the reaction was complete.   On cooling, the product was removed by filtration, and was obtained pure (m. p. 152°–153°) by a single crystallization from alcohol diluted with an equal volume of water.   The yield is nearly quantitative.   From this the difficultly soluble sulphate $(C_6H_5.NC_7H_5O.NH_2)_2H_2SO_4$ was prepared by saponification as directed by Widman.   In the first experiments the free base was obtained from this sulphate and then converted into the soluble hydrochloride.   In the later experiments, however, it was found advantageous to use the orig-inal sulphate, dissolving it in water to which was added just enough alcohol to effect solution.

Four grams of trichlorquinone and 7 grams of α-benzoylphenyl-hydrazine sulphate in a finely divided condition were placed in a flask and 300 cc. of water, 140 cc. of alcohol, and a few drops of sulphuric acid added.   The flask was connected with a return condenser and the contents boiled for five minutes.   The red powder which separated was then filtered from the hot liquid and dried on a clay plate (yield 5 to 6 grams).   The body was

[1] Monograph " Ueber asymmetrische Secundäre Phenylhydrazine," published by the " Gesellschaft der Wissenschaften" at Upsula 1893; also *Ber. d. chem. Ges.,* **26,** 945.

easily purified by crystallizing from benzene, or from benzene-ligroin.   Melting-point 158.5°.

   1. 0.1641 gram substance gave 0.1668 gram silver chloride.

   2. 0.2115 gram substance gave 0.2127 gram silver chloride.

   1. 0.2397 gram substance gave 0.4714 gram carbon dioxide and 0.0620 gram water.

   2. 0.2484 gram substance gave 0.4891 gram carbon dioxide and 0.0619 gram water.

	Calculated for $C_{19}H_{11}N_2O_3Cl_3$.	Found. I.	2.
C	54.09	53.63	53.69
H	2.63	2.87	2.76
Cl	25.23	25.13	24.86

α-Benzoyl phenylhydrazino trichlorquinone is a bright red crystalline body, readily soluble in hot benzene and alcohol, from each of which it crystallizes in long rectangular prisms or in star-shaped groups of small prisms.   It is sparingly soluble in ligroin, and practically insoluble in glacial acetic acid and dilute caustic soda solution.   Its action with phenylhydrazine is similar to that of quinone, decomposition occurring with evolution of gas.   By dissolving in concentrated sulphuric acid as well as by the action of alcoholic potash, the benzoyl group is split off, but some further reaction takes place forming a dark brown crystalline body.   This is soluble in caustic soda and melts with decomposition at 198°.   Its structure has not yet been determined.

NOTE ON A METHOD OF STANDARDIZING WEIGHTS.

BY THEODORE WILLIAM RICHARDS.

ALTHOUGH nowadays it is possible to procure, for a comparatively small sum, sets of weights which are reasonably exact, it is recognized that for gravimetric work demanding any considerable degree of accuracy, corrections on account of occasional errors in the weights must be applied.   It is obvious, moreover, that if the relative values of the weights in an inexpensive box are known, this set may serve a purpose which would otherwise demand a much more expensive one.   For ten years every student in quantitative analysis at Harvard has been required to standardize his weights; and since the method

adopted has some peculiarities, not described in the usual directions for this purpose,[1] it is explained below. This method does not pretend to be especially original ; the reason for its publication is simply a desire to advance the cause of accuracy.

According to our method the weights to be standardized are weighed wholly on one side of the balance, the comparison being made by substitution. This procedure, of course, eliminates a possible inequality in the length of the arms of the balance, which must otherwise be computed. A more important advantage is the fact that it also obviates the mental confusion resulting from the continual interchanging of weights between the opposite pans. Thus is avoided one of the common sources of error in the beginner's work.

It is, of course, necessary that all of the fractional weights should, taken together, constitute a gram ; and because the milligram weights are never used. it is convenient to add an extra centigram weight from another set to supplement the other small weights. The different weights of the same denomination should be marked in a recognizable way, and should always be arranged in the same order in the box. The comparison usually begins with centigrams and proceeds upwards. One of the centigram weights is placed upon the *left-hand* scale-pan, and is balanced by any suitable tare, care being taken that the rider is not too near either end of its path.[2] The zero point of the balance need not have been taken in the first place. The swings of the balance with its centigram load are now carefully noted and then another centigram weight is substituted for the first. Obviously, the amount by which the rider must be moved to attain the same position of equilibrium gives at once the difference between the two weights ; and even the neophyte could hardly err as to its sign. Of course, instead of moving the rider, the difference may be calculated from the change in the swings ; or both swings and rider may be used. The first weight is then replaced upon

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[1] For the usual method adopted by Kohlrausch, see Ostwald's Handbook of Phys. Chem. Measurements (Walker), p. 41.

[2] A crude set of weights is, of course, the most convenient tare, and a 5 milligram weight may be kept on the left-hand pan so that the rider may assume a convenient position. The use of the *left-hand* scale-pan for the weights to be standardized renders a confusion of the sign of the correction less likely, because the rider is on the right. In this case, the *weights are the objects to be weighed*, and hence naturally take the left-hand position.

the left-hand pan, and if the swings correspond to the first obser-
vation it is reasonably certain that the balance has remained in
a constant condition throughout the trial, and hence that the
difference between the two weights has been accurately deter-
mined.   In this way every weight is compared with every other
weight of the same denomination, as well as with the combina-
tion of all the smaller weights.   Thus are obtained a number of
independent equations one less than the number of weights;
and by assuming the value of any one of the weights the others
may all be calculated.[1]

We have found it most convenient for the purposes of calcu-
lation to make the temporary assumption that the first centigram
weight is correct.   From it by the simplest possible process of
addition and subtraction may be built up quickly the values of
all the other weights.   While the values thus computed are
wholly consistent among themselves, they are usually far too
different from the face values of the weights for convenient use.
The reason of this is because the assumed standard is so small a
quantity.   It is necessary then to translate these consistent
values into other terms by dividing every value by the value of
one of the larger weights, to be taken as the new and permanent
standard.[2]

This division (which would demand six or seven place logarithm
tables for the larger weights) is conveniently replaced, however,
by a simple method depending upon the properties of small
numbers in presence of large ones.[3]   It is quite sufficiently
accurate to compare the value of each weight with the correspond-
ing aliquot part of the value of the weight to be taken as a final
standard.   The difference between the actual value and the ideal
value will give at once the correction to be applied to the weight.

[1] Of course, many extra equations, which are not independent of the others, are ob-
tained by the literal fulfilment of the preceding directions. These extra equations may
be used to verify the final results, if desired. The comparisons best suited for the cal-
culation are given in a table on a following page.

[2] If it is desired to refer the whole box of weights to the international standard, it
is, of course, necessary to include a weight which has been standardized at Washington
in the series, and thus to find the value of the international gram in terms of the centi-
gram chosen as the temporary basis. The aliquot parts or multiples of this value are
then used precisely in the manner indicated further on. For all ordinary purposes,
however, this is wholly unnecessary; and one of the 10-gram pieces of the box is a more
convenient standard.

[3] Nernst und Schoenfliess Math. Behand. der Naturwiss, p. 303 (1895).

Of course, if the weight is not heavy enough this correction carries a *minus* sign, and must be *subtracted* from the result of any weighing in which that weight is used; for the deficiency necessitates the addition of extra weight on the rider-arm, and hence the sum of the face-values of all the weights used is too large. Long experience has shown that the sign of the final correction is the most insidious cause of error in the whole process; for the beginner always thinks that if a given weight is too light, its correction should be *added*.

The table below presents all the data and results of a sample standardization, as well as all the calculation which need be written down by anyone possessing even a moderate ability to add figures mentally. In the first column the weights are named by their face-values, which are enclosed in parentheses in order to show that they do not signify true grams. In the second column are given the results of the mutual comparison of these weights copied from a note-book in which every detail of each weighing was recorded. The third column gives the actual values of the weights based upon the first centigram weight; these values are obtained by simply adding together the appropriate preceding values in the third column and the last minute fractional weight enumerated in the second column. The aliquot parts of the value for the 10-gram piece, which is now to be taken as the permanent standard, are recorded in the fourth column, while the corrections sought, obtained by simply subtracting the numbers in the fourth column from those in the third, are given in the last vertical row.

Nominal values.	Data obtained by substitution method.		Preliminary values (actual).	Aliquot parts of 10.01768 (ideal).	Corrections in milligrams (actual minus ideal).[1]
		Grams.	Grams.	Grams.	
(0.01) =	Standard of comparison		Standard	0.01002	—0.02
(0.01′) =	(0.01)	+ 0.00006	0.01006	0.01002	+0.04
(0.01″) =	(0.01′)	— 0.00001	0.01005	0.01002	+0.03

[1] Owing to neglected fractions the figures in the last column, when added together, are sometimes slightly discordant with those given in the second column. This is inevitable; of course such corrections should always be calculated to one decimal place beyond the figure which one wishes to have exact.

Nominal values.	Data obtained by substitution method.		Preliminary values (actual).	Aliquot parts of 10.01768 (ideal).	Corrections in milligrams (actual minus ideal).[1]
		Grams.	Grams.	Grams.	
(0.02)	= (0.01) + (0.01′)	—0.00001	0.02005	0.02004	+0.01
(0.05)	= (0.02) + etc.	—0.00007	0.05009	0.05009	±0.00
(0.1)	= (0.05) + etc.	—0.00006	0.10019	0.10018	+0.01
(0.1′)	= (0.1)	+0.00001	0.10020	0.10018	+0.02
(0.2)	= (0.1) + (0.1′)	—0.00004	0.20035	0.20035	±0.00
(0.5)	= (0.2) + etc.	—0.00011	0.50088	0.50088	±0.00
(1)	= (0.5) + etc.	—0.00004	1.00183	1.00177	+0.06
(1′)	= (1)	—0.00002	1.00181	1.00177	+0.04
(1″)	= (1)	—0.00006	1.00177	1.00177	±0.00
(2)	= (1′) + (1″)	+0.00025	2.00383	2.00354	+0.29
(5)	= (2) + etc.	—0.00040	5.00884	5.00884	±0.00
(10)	= (5) + etc.	—0.00040	10.01768	10.01768	Standard.
	etc.		etc.	etc.	etc.

It is convenient to prepare from the individual corrections a card exhibiting at once the corrections corresponding to the usual combinations of weights from 1 to 99 centigrams and from 1 gram upwards. This card minimizes both the labor of applying the corrections and the danger of possible error in the process. It is hardly worth while to print here an example of such a card, but the method of application may be illustrated. The page of the note-book is ruled with two parallel vertical lines, which contain the two corrections found in the card. The upper correction corresponds in each case to the whole grams, and the lower to the fractional weights.

	Observed weight. Grams.	Cor. mg.	Corrected weight. Grams.
Weight of crucible + substance ·	19.3105	$\left\{ \begin{array}{c} +0.39 \\ -0.01 \end{array} \right\}$	19.3109
" " " alone........	16.9916	$\left\{ \begin{array}{c} +0.06 \\ +0.06 \end{array} \right\}$	16.9917
Weight of substance			2.3192

Thus the increased accuracy is gained with very little sacrifice of time or mental labor. It is usually more convenient to adjust the rider by filing to exactly 12.0 (or 10.0) milligrams rather than to apply a correction for this also.

1 See foot-note, p. 147.

The method of comparing the actual value with an ideal one is also a convenience in standardizing burettes by means of the Ostwald "calibrator." In the original description of this process it is assumed that the calibrator delivers exactly an integral number of cubic centimeters ;[1] but if only a few instruments are to be calibrated it is both troublesome and expensive to secure such a precise instrument. We have found it convenient to use a calibrator of any size, and to compare in parallel columns its multiples with the actual readings of the burette. The capacity of this calibrator is most conveniently obtained in the following manner. Suppose that as a mean of several comparisons it has been found that sixteen fillings of the calibrator correspond to 49.53 cc. on a given burette. Grease is the most serious foe to accuracy in this process. The burette is now refilled, and exactly this amount of pure water is run out into a weighed flask, with all the precautions which would be used in an actual titration. The weight of the water gives by appropriate calculation[2] the true volume of sixteen fillings of the calibrator. Suppose this was found to be 49.44 cc.; then the volume of the calibrator as it is actually used in a calibration must be $\frac{49.44}{16} =$ 3.090 cc. The differences between the successive readings of the burette and the successive numbers 3.09, 6.18, 9.27, ···· etc., give at once the errors of the graduation of the tube at these intervals. These differences or corrections may be plotted on a diagram in which the ordinates are volumes and the abscissas corrections. The correction to be applied for 50 cc. is obviously —0.09 cc. Here again the sign is somewhat perplexing to the inexperienced.

These simple methods have stood the test of years of use in our first course upon quantitative analysis, and their practicability under these circumstances shows that reasonable accuracy in weights and measures is within the easy reach of all.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
February 20, 1900.

[1] Ostwald : Handbook of Phys. Chem. Measurements (Walker), p. 87 (1894).
[2] This Journal, 21, 527 (1899).

METHODS FOR THE DETECTION OF "PROCESS" OR "RENOVATED" BUTTER.

BY W. H. HESS AND R. E. DOOLITTLE.

" "PROCESS" butter commonly called "renovated" butter- is a product prepared about as follows: Unsalable dairy or creamery butter, bought at a low price in the spring and summer, is melted and the butter-fat drawn off. The curd originally present in the butter is rejected, thereby removing a large part of the rancidity if any be present. Milk is now added to this butter-fat and stirred in so as to be evenly mixed throughout, when the whole mass is cooled quickly, so as to prevent the separation of the "butter oil." This milk soon sours, the casein therein is coagulated, and thus there is provided an artificial curd which contains a percentage of nitrogen about the same as that of the curd of real dairy butter. The butter-fat of this renovated butter does not materially differ from ordinary butter-fat in any of its chemical properties.

It is evident, therefore, that for the detection of process butter, we must depend on the difference between the curd of genuine butter made from cream, and the artificial curd supplied in "process" butter by the addition of milk. There are proteids in milk which are insoluble in water, and therefore separate out and occur with the cream. The insolubility of these proteids was more fully brought out by S. W. Babcock in his work upon the proteids of cream (1888). These proteids, insoluble in water, pass into the butter and form the main part of the substance commonly known as the curd. It is a cohesive, gelatinous mass and notably non-granular. The curd of "process" butter, however, consists chiefly of coagulated casein. This is a flaky, granular, non-cohesive mass, and does not, therefore, resemble the proteids of cream in physical properties. The following method of analysis has proved satisfactory :

TEST FOR BUTTER-FAT.

The purified fat is examined with the butyro-refractometer. At 25° C., the reading seldom varies from 51° in the case of "process" butter, and hence does not differ from butter-fat in

this respect.   This reading is taken to assure the operator that the fat at hand is butter-fat and not a substitute, as oleomargarine. A determination of the volatile fat acids will serve as well.

TESTS OF THE CURD.

After having proved that the fat is butter-fat, an examination of the curd is made.   The first test that is made is one which depends on the cohesive properties of the curd of pure butter. If a portion of the butter sample, about 1 gram, is placed in a convenient container—a spoon answers the purpose admirably— and heated over a free flame, the mass will, in case the sample is pure butter, assume a foamy appearance, which is very striking. In case the sample is "process" butter, no foaming is produced, but the mass merely bumps and sputters like hot grease containing water.   Oleomargarine behaves like "process" butter, but it has been excluded by previous tests.

APPEARANCE OF THE CURD.

A sample of the butter is melted in a beaker, the fat is decanted, and the curd is well washed with ether to remove the remnant of fat.   The curd is poured out on a clean glass plate in a thin layer and allowed to dry.   A sample of genuine butter is treated likewise.   The physical appearance is then quite distinctive especially when a magnifier of 3 to 6 diameters is used for the examination.   The curd from the true butter will have an amorphous, non-granular appearance, while the curd from "process" butter has a very coarse, curdy appearance. The one is the proteid of cream, the other is the proteid of milk; the one is a gelatinous, ropy mass, the other is a granular, easily divided substance.   Casein dissolves readily in acid or alkali; the curd of genuine butter dissolves only on prolonged treatment with these reagents.

IDENTIFICATION OF THE SOURCE OF THE CURD.

A convenient sample of the butter, 25 to 100 grams, is placed in a beaker and melted at 45° to 50° C.   (It is worthy of note that "process" butter will not yield a clear liquid fat at the end of half an hour or even twenty-four to forty-eight hours, while genuine dairy or creamery butter yields a clear supernatant liquid as soon as melted.)   As much as possible of the fat is

decanted, and the remaining portions, composed of curd, water, salt, and the remnant of fat, are thrown upon a moistened filter and the water is allowed to drain through. This water carries the soluble proteids as well as salt. To this filtrate, a few drops of acetic acid are added and then the solution is brought to a boil. In case the filtrate is from the curd of pure butter, only a slight milkiness is produced (absence of albumins); but in case the filtrate is from the curd of "process" butter a flocculent, white precipitate of albumins is formed, a certain indication that the source of the curd is from milk. Other tests for the albumins may, of course, be used. If strong hydrochloric acid be added to the filtrate from the curd of " process" butter, a violet color is produced (Liebermann's test for albumin).

QUANTITATIVE EXAMINATION OF THE CURD.

If the artificial curd of "process" butter has been derived from milk, then the ratio of the percentage of casein to the percentage of albumins should be the same as that ratio is in milk, or about 9 parts of casein to 1 part of albumins. The ratio in the curd of "process" butter sold on the market, as actually found, was 8.6 parts of casein to 1 part of albumins. The method of estimation is as follows: 50 grams of the butter are placed in a beaker and dissolved in ether to a clear solution. In case the sample is genuine butter, the curd is so finely divided that it remains in suspension in the ether and considerable time may be required for a clear solution. As much as possible of the ether solution of fat is decanted and the whole of the remainder transferred to a separatory funnel. The casein and water with the salt are then removed and the washing with ether repeated three or more times to remove all the fat from the curd. The casein is then filtered out, washed with water, and the nitrogen estimated by the Kjeldahl method. The filtrate from the curd is made slightly acid with acetic acid and then brought to a boil. The albumins are filtered out and estimated by the same method.

These tests serve to differentiate between genuine butter and " process" butter, as it is now found on the market.

LABORATORY OF THE MICHIGAN DAIRY
    AND FOOD DEPARTMENT.

CHEMICAL METHODS FOR ASCERTAINING THE LIME REQUIREMENT OF SOILS.

By H. J. WHEELER, B. L. HARTWELL, AND C. L. SARGENT.

HAVING recognized the occurrence of an injurious degree of acidity in the upland soils of Rhode Island and other states, even upon steep hillsides, it became important to ascertain by chemical means if possible the relative lime requirement of different soils. If such could be done in a simple and effective way, then one would be in a position to recommend satisfactorily what amount of lime to use per acre without resort to field tests.

TESTS BY BLUE LITMUS PAPER.

Perhaps the simplest, though nevertheless a very satisfactory test, is that made by bringing a piece of blue litmus paper in contact with the moistened soil and observing the intensity and rapidity of the reddening thus produced. Though unsatisfactory, in view of its not being a quantitative test, much valuable information regarding the amounts of lime which should probably be used, may thus be obtained, after some experience, by one who is a careful observer. Wahnschaffe[1] in speaking of this reaction says, "since the free carbonic acid of the soil reddens the paper, one must allow it to dry and observe whether or not the red color is still visible." Roscoe and Schorlemmer[2] state that "carbonic acid readily decomposes into water and carbon dioxide. In consequence of this, litmus paper which has been turned red in the aqueous acid, becomes blue on drying." They then immediately add that the reddening of litmus solution may be brought about by conducting into it carbon dioxide, but that upon heating the solution the carbon dioxide is expelled, and after boiling a few seconds the liquid again becomes blue. In Watts' Dictionary of Chemistry[3] it is stated that an "aqueous solution of CO_2 turns blue litmus paper wine-red ; the blue color returns on exposure to air." It seems probable that on account of the well-known reaction of litmus solution whereby, when reddened by carbon dioxide gas, it returns to a blue color, it has

[1] Anleitung zür wissenschaftlichen Bodenuntersuchungen, Berlin (1887), p. 56.
[2] " Treatise on Chemistry." I, New York (1888), p. 638.
[3] Vol. I, London (1890), p. 695.

been assumed that a similar reaction would necessarily take place when operating with litmus paper. This conclusion seems exceedingly probable since the writers have been unable to find references in the literature to any definite tests bearing upon this point. It is possible also that tests, if made, were carried out by operating with carbonic acid upon small sections of a piece of litmus paper, in which case, sufficient alkali might diffuse from the surrounding paper into the section acted upon, to neutralize the carbonic acid still remaining. That such a return of the blue color may result when the entire portion of the litmus paper is not subjected to treatment with acid, has been demonstrated by us upon commercial paper in the case of carbonic acid and of very dilute citric acid.

Owing to the action of the fingers upon blue litmus paper and the bleaching action of the sun, the test would be far simpler and more reliable in the hands of practical farmers if it were not necessary to wait for the paper to dry before drawing conclusions as to the probable needs of the soil. In view of the fact that some of the conditions prevailing when working with litmus paper are so different from those existing when employing the solution, it seemed probable that blue litmus paper, if entirely reddened by carbonic acid, and dried with the promptness that would ordinarily be expected, would not return to its original blue color. Dr. H. E. Stockbridge told one of us that he was under the impression that he once found this to be the case. In order to test this matter thoroughly, trials were made with ordinary commercial blue litmus paper and also with lots of paper prepared from solutions made according to Classen[1] and Sutton.[2] The carbonic acid was prepared by expelling the carbon dioxide from an aqueous solution of chemically pure sodium bicarbonate by simply boiling without the use of acid. A return condenser was employed and the carbon dioxide was washed in distilled water before its collection. Steam, generated from the distilled water which was used subsequently to dissolve the sodium bicarbonate, was first passed through the entire apparatus for some time and the distillate tested to insure the absence of

[1] Böckmann's "Chemisch-technische Untersuchungsmethoden", Vol. I, Berlin (1888), p. 97.

[2] The third method. Sutton's "Handbook of Volumetric Analysis", London (1882), p. 31.

volatile organic acids. Treated with carbonic acid prepared in this way all three lots of blue litmus paper were permanently reddened when dried naturally in the open air or in a room free from acids and ammonia. It is evident therefore that when dried naturally the carbon dioxide is not lost to any great extent or else the red, acid coloring-matter of the litmus is too firmly fixed upon the fiber of the paper, to permit of its reunion with the base, a change which would have resulted in the case of a solution, after the expulsion of the carbon dioxide. Coupling with these results the fact that so long as a liberal amount of calcium carbonate is present in a soil, the presence of carbonic acid tends to increase rather than lessen the tendency toward an alkaline reaction[1] (a point proved by us experimentally in the laboratory) it must be evident that the indication of acidity afforded by a piece of blue litmus paper is sufficient to show a deficiency of calcium carbonate or other basic ingredients in soils, without first allowing the paper to dry, as suggested by Wahnschaffe.

TESTS BY EXTRACTION WITH AMMONIA.

Müntz[2] states that it is easy to distinguish whether or not a soil is acid, since if such is the case it imparts a black color to ammonium hydroxide when the two are brought in contact. He adds that in the case of soils which are not acid, the organic matter is in an insoluble combination with lime and consequently yields nothing to ammonium hydroxide. The same has been found by us to be the case with a sample of fertile adobe soil kindly forwarded by Professor Goss, from New Mexico. Similar observations have also been made on one Massachusetts and two Rhode Island soils where wood ashes or calcium carbonate in some form had been applied to the land with such frequency as to entirely overcome its acid reaction upon blue litmus paper. Snyder,[3] however, calls attention to a soil which he says contained 3.15 per cent. of lime (CaO) and 4.19 per cent. of carbon dioxide, and yet when treated with ammonium hydroxide for the determination of the so-called "free humic acid" yielded a dark brown extract amounting to from 0.3 to 0.4 of a

[1] Compare Detmer Die naturwissenschaftlichen Grundlagen d. allg. landw. Bodenkunde (1876), p. 451; also Stöckhardt, Jahrbuch für Agriculturchemie (1866), p. 10.

[2] Encyclopédie Chimique, 4, Pt. 4, p. 18.

[3] Bulletin No. 56, Chemical Division, United States Department of Agriculture, Washington, D. C., 1899.

per cent.   This would tend to throw some doubt upon the
reliability of the treatment with ammonium hydroxide as a means
of arriving at the lime requirements of all soils, though it is not
improbable that for soils of certain sections of the United States
which are possessed of definite characteristics, the treatment may
be of considerable value as was the case in the particular acid
soils, for which Müntz employed the method.   The details of
the method as proposed by Müntz[1] are as follows :   To 20 grams
of powdered soil, add 50 cc. of concentrated ammonium hydroxide.
Allow it to stand for from two to three days in a warm place.
Agitate frequently and at the end of the period make the volume
up to 1 liter.   It is then shaken and allowed to subside for
twenty-four hours.   To 500 cc. of the liquid add sufficient
hydrochloric acid to give a strong acid reaction in order to pre-
cipitate the humus, which carries with it some mineral matter.
After the precipitate has subsided, decant the supernatant liquid,
collect on a filter, dry and weigh in a weighing bottle, incinerate,
deduct the ash, and the "free humic acids" are thus obtained
by difference.   In order to determine what influence, if any, the
use of concentrated ammonium hydroxide might have upon the
results compared with dilute solutions, a sample of upland soil
was tested by the above method and yielded 1.00 per cent.
Treated for the same time with the same amount of ammonium
hydroxide previously diluted to 500 cc. (containing 1.13 per
cent. of ammonia) it also yielded 1.00 per cent.   The same soil
treated for a like time with 500 cc. of the same solvent containing
2.4 per cent. of ammonia yielded 1.00 per cent.   Employing
sufficient concentrated ammonium hydroxide so that after
diluting to 500 cc. it would have the same strength as in the last-
mentioned instance, it yielded, treated for the same time, 1.03
per cent.   It appears therefore that in the case of ordinary soils
the strength of the solvent within reasonable limits is not an
essential feature, and that the solution usually employed in total
humus determinations may be used here with equal propriety.

THE METHOD OF HOLLEMAN FOR DETERMINING THE LIME REQUIREMENTS OF STIFF CLAY SOILS.

Holleman[2] in searching for the cause of the occasional

[1] Encyclopédie Chimique, 4, Pt. 4, p. 182.
[2] Die landw. Versuchs-stationen 41 (1892), p. 38.

ineffectiveness of gas-lime upon certain stiff clays in Holland concluded that it might be due to the presence in them of considerable calcium carbonate. He thereupon made determinations of the lime removable by water and by water saturated with carbon dioxide. The water-soluble lime was determined as follows: Twenty grams of air-dried soil were digested with frequent shaking, at ordinary temperature, for forty-eight hours with 1 liter of distilled water. Five hundred grams of the filtrate to which a few drops of acetic acid had been added were evaporated, the residue taken up in water; and first a little acetic acid and then a measured quantity of $\frac{N}{10}$ solution of ammonium oxalate were added and the volume made up to 100 cc. After filtration, the excess of oxalic acid is estimated by titrating with a $\frac{N}{10}$ solution of potassium permanganate. For determining the lime soluble in carbonic acid 20 grams of air-dried soil are taken and sufficient distilled water added to make up 1 liter ; it is then saturated with carbon dioxide and after twenty-four hours filtered and treated as described above. From the data obtained by Holleman, he concluded that where extraction with carbonic acid removed 0.15 per cent., or less, of calcium oxide, stiff clay soils would be benefited by liming.

In order to test the applicability of this method to the acid sandy and clayey loam soils of our State, two samples were selected, the first being from a farm in Warren, R. I., where, with the same manurial and other treatment, the yield of beets upon the unlimed plot was 272 pounds against 329 pounds upon the limed plot. The second soil was from Foster Center, R. I., where under the same conditions the yield of beets upon the unlimed plot had been 36.6 pounds and upon the limed one 143.4 pounds. In making the test of the soil from Warren, 80 grams of soil were employed, and in that from Foster Center, 40 grams. The soil was placed in each case in a flask to which 1 liter of distilled water, saturated with carbon dioxide, was added. The flask was agitated frequently and the treatment continued for forty hours. Four hundred cc. of the extract were evaporated to dryness, taken up in water and a little acetic acid, $\frac{N}{10}$ ammonium oxalate was added, and after filtration, the whole was made up to 200 cc. Aliquot parts of this solution were titrated with $\frac{N}{10}$ potassium permanganate, after acidulation with sulphuric acid. In

one instance the small amount of acetic acid was removed by evaporation to dryness before adding sulphuric acid and titrating without practically affecting the results.   Allowing for the blank found, the amount of calcium oxide thus determined amounted in the Foster Center soil to 0.0360 per cent.   In the case of the Warren soil, which was treated in the same manner, the amount of calcium oxide removed from the soil was found to be 0.0287.

The Warren soil extracted with distilled water, in a similar manner for forty-eight hours, yielded 0.0120 per cent. of calcium oxide.

From these tests it will be seen that the soil which was least benefited by lime, yielded less lime than the other.   It is possible that the use of double the amount of soil in the last instance may have depressed the result somewhat as compared with the other, though it is not likely that the difference caused by this factor would, under the circumstances, have been readily appreciable.   At all events the amount of lime removed in the highest case was only about one-fifth of that below which Holleman found lime useful on stiff clays.

It appears, therefore, in view of the marked degree of acidity of those of our soils which it seemed desirable to test as to their lime requirements, that this method is probably not of great value.   It is regretted, nevertheless, that the pressure of routine work has prevented making further tests of the applicability of the method to our special needs, particularly with greater attention to maintaining the saturation of the carbonated water.

THE METHOD OF TACKE FOR DETERMINING THE FREE HUMUS ACIDS IN THE PEAT (MOORBODEN) SOILS OF NORTH GERMANY.

Tacke[1] states that no method is known for determining quantitatively the acidity of soils, and calls attention to the desirability of possessing a satisfactorily exact method for the purpose.   He discusses the difficulties in the way of determining the acidity by various ways which would naturally suggest themselves, and finally gives a method which yielded good results.   It is impossible to give the method satisfactorily in

[1] *Chem. Ztg.*, No. 20, 1897, p. 174.

detail without reproducing the illustration of the apparatus which he employed. Essentially the method consists in expelling the carbon dioxide from calcium carbonate brought in contact with the soil at ordinary room temperature. Hydrogen is passed over the soil for some time in the apparatus, then finely divided calcium carbonate, shaken up with water, is introduced and allowed to act upon the soil for two and a half hours or longer as desired. The carbon dioxide disengaged is taken as a measure of the acidity of the soil, the amount being determined by passing it through a Pettenkofer tube containing $\frac{N}{5}$ or $\frac{N}{10}$ sodium hydroxide. The liquid is finally removed from the tube, taking care in regard to the absorption of carbon dioxide from the air, barium chloride then added and the solution titrated with $\frac{N}{5}$ or $\frac{N}{10}$ hydrochloric acid using phenolphthaleïn as an indicator with attention to the points brought out by the investigations by Küster[1] and by Lunge.[2] Determined in this way, using soil in its natural state, the amount of acid reckoned as carbonic acid, represented by 100 parts of dry material, amounted in the case of various peat soils to from 1.721 to 2.240 per cent. The method gives promise of much value for such soils as a guide to the amount of lime which they should receive. In April, 1895, experiments were begun by one of us for the purpose of ascertaining if the amount of carbon dioxide liberated from calcium carbonate upon heating it with upland acid soils in the presence of water, could be used as a guide to the amount of lime to apply to them. Owing to the pressure of routine matters, this work was several times taken up and then soon discontinued. Not having satisfactorily perfected a method at the time Tacke's results were published, it was decided to see if his method was applicable to our upland soils. Two unlimed soils were selected for the trial, the one from land where sodium nitrate had been applied for several years and the other from land where the manuring had been identical except that the same quantity of nitrogen had been applied in ammonium sulphate. The yields of most crops had been for several years far better upon the former than upon the latter plot of land.

[1] *Chem. Ztg. Repert*, 29, 282 (1896); *Ztschr. anorg. Chem.*, 13, 127 pp. (1896).
[2] Bestimmung von Caustischen und Kohlensauren Alkalien, G. Lunge, *Ztschr. angew. Chem.*, 41 (1897).

The percentage of carbon dioxide obtained by treat-
ment for three hours, calculated to dry soil, was 0.039 for the
soil which had received sodium nitrate and 0.067 for the one
which had received ammonium sulphate. In other words
the results stood in the same relation as the yields. Taking
into account the fact that the soils contained nearly 4 per cent.
of humus and from 1.25 to 1.55 per cent. of humus immediately
soluble in ammonium hydroxide, it is evident that the action of
this class of soils upon calcium carbonate, at ordinary tempera-
ture, is far less vigorous than that of the peat soils tested by
Tacke. The percentages obtained by this method are so small,
and the element of error proportionately so great, that the indi-
cations are not particularly favorable to its use with soils of the
character to which it was hoped the test would apply.

DETERMINATION OF TOTAL HUMUS.

The determination of total humus could only be expected to
throw light upon the lime requirement of soils where marked
acidity of the soil exists, and while it might even then bear no
relation to the benefit to be derived from liming, it was deemed
of interest to ascertain by actual tests what relation, if any, would
be found. Combined with the tests to determine the amount of
humus soluble in ammonium hydroxide, without previous
extraction of the soil with hydrochloric acid, it was also possible
to learn if there appeared to be any relation between the gain
from liming and the percentage of the total humus, which was
directly soluble in ammonium hydroxide.

The method employed was essentially that of Grandeau as
modified by Huston and McBride.[1] Twenty grams of soil were
first extracted with hydrochloric acid as proposed by Hilgard[2]
with the employment of an automatic washing apparatus, until
no further reaction for lime was obtainable in the wash solution.
After the removal of the acid by successive washings with dis-
tilled water, the material was extracted with ammonium hydrox-
ide, aliquot portions of the extract evaporated to dryness, incin-
erated, the ash deducted and the humus thus obtained by differ-
ence. The relation between the results obtained and the data

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1 Wiley's " Principles and Practice of Agricultural Analysis," Vol. I, 327, 328.
2 *Ibid.*, p. 325.

secured in actual experiments with lime upon several soils will be discussed later.

DETERMINATION OF THE AMOUNT OF LIME REMOVABLE BY HYDROCHLORIC ACID.

In soils containing some calcium carbonate, a number of methods have been proposed for arriving at their probable need of lime.   Among others, Mondesir[1] gives a method by which he proposes to ascertain the active calcium carbonate in soils, since, as he says, soils may contain considerable of this substance, perhaps so surrounded by particles of clay that for practical purposes it is of little or no use, and nevertheless stand in need of lime. In our own soils which have been shown to contain practically no calcium carbonate, it must be evident that such methods can be of no avail.   If the need of lime, in soils of the character under consideration, is determinable by the quantity of lime present, regardless of its form, then extraction with a strong mineral acid ought to serve as a fair basis for arriving at the lime requirement of the soil.   Various methods of treatment, with different kinds, strengths, and volumes of acids have been proposed.   For the purpose in hand the method[2] of the Association of Official Agricultural Chemists of the United States was followed, the digestion of the soil (10 grams) having been carried on for ten hours with 100 cc. hydrochloric acid (1.115 sp. gr.) at the temperature of boiling water with the employment of a return condenser. The data thus secured, with soils tested in a practical way with lime, in the field, are given later in tabular form in which connection they will be discussed.

ACIDITY BY TITRATION.

If means could be devised for determining the relative acidity, or the lime requirements of soils by titration, the matter would be rendered extremely simple and the tests could be made in great numbers at small expense.   Owing to the extreme insolubility of the acids, or acid compounds of the soil, the titration of a watery extract of the soil could not be expected to furnish any very valuable data.   In order to obtain, if possible, results which might indicate in some measure the probable affinity for lime

[1] Annales de la Science Agron., 2, 270 (1887).
[2] Bull. 46, Div. of Chemistry, U. S. Dept. of Agriculture, pp. 39, 40.

(the substance which would usually be applied in the neutralization of soils), a study was made of the action of lime-water, the strength of the supernatant liquid, after contact with the soil for some time, being determined by titration.   Air-dried soil was employed so as to eliminate any possible influence which might arise from drying at higher temperatures.   Owing to the fact that these trials were only preliminary, and on account of the slight variation in the moisture of the soils examined which varied but little from 2.25 per cent., no correction has been applied to the results for the moisture contained in the soil itself. Ten grams of air-dried soil were brought in contact with 50 cc. of lime-water in a small flask.   The flask was securely corked and occasionally agitated.   At the end of about twenty hours the supernatant liquid was passed rapidly through a dry filter, an excess of hydrochloric acid of known strength (3 cc. neutralizing 36.1 cc. of the lime-water) added and the amount of unneutralized acid determined by titration with lime-water.   In this way the volume of lime-water neutralized by 10 grams of the air-dried soil was indirectly determined.   With the same soil more lime-water was required, without exception, where it had remained unlimed, than where lime had been applied.   In the comparison of two unlimed soils manured alike excepting that one had received its nitrogen for several years in sodium nitrate and the other in ammonium sulphate, the differences in the amounts of lime-water neutralized were not always in harmony with, nor were they marked enough to accord at all with the experience obtained in tests of the soils made by plants themselves.   In a comparison of limed and unlimed soils it was found that by employing a greater amount of lime-water (75 cc.) greater differences were obtained than by the use of but 50 cc. Possibly the use of even a somewhat greater amount would have given even better comparative results.   Trials were also made, employing hydrochloric acid twenty times as dilute as that first tried.   Coralline was used as an indicator, and though far from satisfactory in some respects, it was the only one tried which proved at all effective.

The preliminary trials not having indicated any particular general value of such a method, a trial of ammonium hydroxide was next made.

TITRATION TESTS BY MEANS OF AMMONIUM HYDROXIDE.

A number of preliminary tests gave indications that the use of ammonium hydroxide in place of lime-water, was capable of giving results more nearly in accord with those obtained by plant tests. The method finally used was as follows : Fifteen grams of air-dried soil were placed in a glass flask and 100 cc. of about $\frac{N}{15}$ ammonium hydroxide and 100 cc. of distilled water added. This was allowed to stand at the ordinary temperature of the laboratory for about forty-two hours, with frequent agitation during the earlier portion of the time. After it had finally been allowed to settle, a definite amount of the supernatant liquid was treated with hydrochloric acid (about $\frac{N}{2}$) at the rate of five cc. for each 20 cc. of the liquid, and made up to a given volume. After the precipitated humus had subsided, aliquot portions of the solution (50 cc.) were titrated with ammonium hydroxide, using coralline as an indicator. Since by this treatment some portion of the organic acids may be dissolved by the ammonia, the method cannot give an absolute idea of the acidity of a soil. On the other hand, a method which determines the humus immediately soluble in ammonium hydroxide before extraction with hydrochloric or other strong acid, gives no indication of the acidity represented by acid inorganic compounds. Possibly if the amount of humus soluble in ammonium hydroxide were determined, and likewise the amount of ammonia held at the same time in combination by the insoluble residue, the combined data might furnish a better guide than either one alone. Unfortunately the occasional opportunities available for conducting such investigations have not yet permitted a study of this question.

In order to ascertain what effect a variation in the strength and volume of the ammonium hydroxide and the volume of soil might have, a given[1] soil was tested in various ways.

(1) Twenty grams of soil were treated with 100 cc. of ammonium hydroxide diluted with a like quantity of water.

(2) Twenty grams of soil were treated with 50 cc. of ammonium hydroxide diluted with 150 cc. of water.

[1] Berthelot and André (*Ann. chim. phys.*, 7th Séries, 1, 286 (1894)) in operating upon organic residues from soils treated with hydrofluoric acid, state that the amount of potassium oxide held by the organic matter varied with the strength of the potassium hydroxide with which it was treated.

(3) Twenty grams of soil were treated with 200 cc. of ammonium hydroxide.

(4) Twenty grams of soil were treated with 150 cc. of ammonium hydroxide.

(5) Fifteen grams of soil were treated with 100 cc. of ammonium hydroxide.

The following were the amounts of ammonium hydroxide retained in combination by the soil calculated in each case to 10 grams of substance.

	Ammonium hydroxide. cc.
(1)	14.3
(2)	11.1
(3)	13.5
(4)	14.0
(5)	13.7

It will be seen from a careful examination of the data that they give some indication that only the weakest solution materially affected the results.

The trials of a number of Rhode Island soils by this method as described on page 170 are given in a subsequent table where the data may be compared with those obtained by other chemical methods and with the actual gains in yield of beets, obtained by the employment of lime.

METHOD FOR DETERMINING THE LIME REQUIREMENT OF SOILS BY COMPARING, UNDER IDENTICAL CONDITIONS, THE COLOR OF AN AMMONIUM HYDROXIDE EXTRACT OF SOILS OF UNKNOWN CHARACTER WITH ONE OF KNOWN CHARACTER.

The method employed was to treat in a warm room like amounts of soil with like volumes of ammonium hydroxide (containing about 2.4 per cent. of ammonia) for two days with occasional agitation. The small amount of water contained in the air-dried soil itself has been shown to exert no appreciable effect upon the result so that for approximate comparisons, drying a portion of the soil at a high temperature and making allowances for the water in the soil, is unnecessary. The colors of the solutions are finally compared and if darker than the standard, they are diluted with water to match it, or if lighter in color some of the standard solution prepared from the

soil of known character, is similarly diluted until it matches the one with which the comparison is being made. The amount of dilution in either case measures the excess or deficiency of color as compared with the standard. It was thought that certain weighable matters might be extracted by ammonium hydroxide from unhumified plant residues which might not color the solution to the same extent as the matter which is actually humified. In such a case, this method might perhaps give better indications than that as employed by Müntz (see page 155). The possible variation in color of the individual ingredients of the complex, which is classed as humus, may in some cases seriously interfere with the use of the method.

The rapidity with which a large number of comparative determinations can be made after the material has settled, is a strong point in its favor.as compared with the method of Müntz. The results obtained by both methods may be compared below in connection with those obtained in actual plant tests upon limed and unlimed soil.

ATTEMPTS TO DETERMINE THE LIME REQUIREMENT OF SOILS BY MEASURING THE CARBON DIOXIDE EXPELLED UPON HEATING A GIVEN QUANTITY OF SOIL, IN THE PRESENCE OF WATER, WITH CALCIUM CARBONATE OR WITH SODIUM CARBONATE.

This work was begun in April 1895, at which time Tacke's method of treating peat soils at ordinary temperatures with calcium carbonate, had not been published. No notice of similar attempts to arrive at the lime requirement of soils having been found, the line of work was apparently wholly new and had to be conducted without the aid of any previous experience.

The first soil selected for this work was from the permanent experimental plot No. 23, which had been manured annually beginning with the year 1893, with the following commercial materials ; viz., dissolved bone-black, potassium chloride and ammonium sulphate. The same arrangement was employed for the absorption of the carbon dioxide as is customary in ordinary determinations of carbon. As a preliminary trial 40 grams of soil, containing 24 per cent. of water capable of being driven off at 100° C., were placed in a Wolff flask and heated, in the

presence of water, with 4 grams of calcium carbonate. On account of the rapid evolution of carbon dioxide, the heating had to be conducted with the utmost care, as the boiling-point was approached, in order that the gas might be entirely absorbed.

A blank test with a definite amount of water and 80 grams of the soil (passed through a sieve containing holes $\frac{1}{25}$ of an inch in diameter) gave 0.0124 gram of carbon dioxide. A blank test with the water and 8 grams of calcium carbonate yielded 0.002 gram of carbon dioxide. Assuming that no carbon dioxide came from the calcium carbonate, 80 grams of the soil must have yielded upon heating in the manner described but (0.0124–0.002) 0.0104 gram of carbon dioxide.

Eighty grams of soil were heated with the same amount of water and calcium carbonate, and kept at the boiling-point until the evolution of gas seemed to have become practically constant and but very limited in amount. The carbon dioxide yielded, amounted to 0.338 gram. Assuming again that the entire blank from the water and calcium carbonate was due to the water and deducting therefore the blank of 0.0124 gram, it is seen that the amount of carbon dioxide found to have been liberated as a result of the action of the calcium carbonate upon the 80 grams of soil, was 0.3256 gram. Owing to rapid evolution of gas on approaching the boiling-point, which necessitated the frequent removal of the lamp, it was feared that some carbon dioxide must have passed through the entire apparatus.

A subsequent test with 40 grams of soil and 8 grams of calcium carbonate was then made. Deducting a blank of 0.0052 gram for the soil and 0.002 gram for the water and calcium carbonate, the amount of carbon dioxide expelled by the soil was found to be 0.1762 gram. This corresponds to 0.3524 gram for 80 grams of soil as compared with 0.3256 gram in the first test, but in the last test great care was exercised that no carbon dioxide should be lost.

A third test with 40 grams of soil and 4 grams of calcium carbonate yielded 0.178 gram of carbon dioxide. Deducting, as above, a blank of 0.0072, the amount of carbon dioxide found to have been liberated by the soil was equivalent to 0.3416 gram for 80 grams of soil.

In order to ascertain if differences between soils corresponding

to those shown by the growth of plants could be detected, a soil (from permanent Plot No. 27) was selected which had been manured the same as the other excepting that it had received its nitrogen in sodium nitrate instead of in ammonium sulphate. A blank test with 40 grams of soil and with the usual amount of water yielded 0.015 gram of carbon dioxide. A test with 40 grams of soil gave, after deduction of the blank just mentioned, 0.1402 gram of carbon dioxide or the equivalent of 0.2804 gram for 80 grams of soil, or much less than was shown by the soil first tested. This accorded with the results secured in plant tests and indicated much greater acidity where nitrogen in ammonium sulphate had been employed than where nitrogen in sodium nitrate was used, or where a basic instead of an acid residue had been left in the soil. In all of the tests thus far made, the operation was stopped after the chief evolution of gas was apparently over and when only a constant and very slight evolution was still noticeable.

To ascertain the effect of longer heating, 40 grams of soil and 4 grams of calcium carbonate were treated for a much longer time than heretofore. The amount of calcium oxide eliminated, allowing for the blank of 0.015 gram was equivalent for 80 grams of soil to 0.3126 gram as compared with 0.2804 gram where the period of heating was less prolonged. Another test was made under the same conditions, continuing the heating for about the same period as in the preceding instance. The net amount of carbon dioxide driven off, per 80 grams of soil, amounted to 0.322 gram. The same material brought to boiling once more and heated for some time yielded, per 80 grams of soil, 0.032 gram of additional carbon dioxide. Brought to boiling and heated for a third time the further loss for the same amount of soil was equivalent to 0.0256 gram. From these tests it appeared probable that beyond a certain point the attack upon the calcium carbonate became very limited or that a gradual oxidation or else a splitting up of the organic matter was taking place. To ascertain if this would go on at an appreciable rate at ordinary temperatures, a current of air was next passed for two and one-half hours over the material which had been thus successively heated. As a result it was found that no weighable amount of carbon dioxide had been eliminated. Further heating, as

before, resulted in a still further elimination of carbon dioxide and an increase in the weight of the absorption tubes. From this it was evident that there was apparently no reasonable time limit within which the elimination of carbon dioxide would be ended, and hence to obtain satisfactory comparative tests with different soils, the period of treatment, temperature, and other conditions must all be kept as uniform as possible. One apparent drawback to the method as it was used, was the necessity of conducting the heating so cautiously, and in consequence, for so long a time, in order that the carbon dioxide might all surely be absorbed, for by doing so the opportunity for the gradual breaking up of the organic matter was much increased. To overcome this objection, in a measure, the use of soda-lime was resorted to as an absorbent for carbon dioxide. By this means, less care was required to insure the absorption of the gas and the period of heating could be materially reduced. Nevertheless the method was still unsatisfactory, and in consequence, it was proposed to operate so as to subject the material to the action of heat a minimum length of time and either measure the volume of the carbon dioxide disengaged or to determine it indirectly by titration with the employment of barium hydroxide, or by estimating the amount of carbonate formed from it and so indirectly the carbon dioxide. Preliminary to this work it was thought wise to ascertain if possible the minimum time that it was necessary to heat the calcium carbonate and soil, in the presence of water, to insure that all of the humus had united with calcium oxide. It is well known that in many cases where soil contains naturally considerable quantities of lime and magnesia, ammonium hydroxide extracts practically no humus until the lime and magnesia have first been removed by acids. Such has been found to be the case in soil from New Mexico and with certain soils from Massachusetts and Rhode Island, which had been treated successively with calcium carbonate. The idea therefore suggested itself that by heating a number of soils with calcium carbonate and water for varying intervals of time, and subsequently testing the residues with ammonium hydroxide, it could be ascertained how long it was necessary to continue the heating in order to get practically all of the humus into an insoluble combination with lime. It was thought that this time

might be safely taken as the limit for continuing the heating and that the amount of carbon dioxide thus disengaged would serve as a suitable measure of the lime requirement of soils. It was also proposed to test the method with soils which do not react acid, in order that further light might be thrown upon the probable applicability of such a method to the purpose in hand. Unfortunately, routine work has prevented the further carrying on of this investigation. It is a question of too great scientific and practical interest to be laid aside at this point, and it is hoped that opportunity for further pursuit of the question will be afforded in the near future.

COMPARISON OF THE GAIN IN BEETS, RESULTING FROM THE USE OF LIME, WITH THE DETERMINATION OF THE LIME REQUIREMENT OF SOILS MADE BY VARIOUS CHEMICAL METHODS.

The following table shows the amounts of beets produced upon limed and unlimed soil in different sections of Rhode Island. Each plot was manured alike with commercial nitrate of soda, muriate of potash and dissolved bone-black. The table gives the percentage gain from liming, also the amount of humus immediately soluble in ammonium hydroxide, the percentage of "total" humus, the amount of calcium oxide removable by extracting with strong mineral acid, the number of milligrams of nitrogen in the ammonia held in combination by 10 grams of soil, the comparative dilution of the ammonium hydroxide extract of a soil of known character to give a degree of coloration corresponding to that exhibited by the extracts from the different soils tested, the amount of calcium oxide removable by carbonated water and the percentage of material in the respective soils which was so coarse as not to pass a sieve with openings $\frac{1}{15}$ of an inch in diameter. Only such material as passed circular openings of this size, was employed in the various tests.

The analytical data in the table were obtained with soil passing a sieve with hole $\frac{1}{15}$ of an inch in diameter. The results are calculated to dry soil.

Locality.	Yield of table beets. Unlimed plot.	Yield of table beets. Limed plot.	Percentage gain in yield (of beets) from liming.	Total humus.[1]	Humus immediately soluble in ammonium hydroxide.[2]	Percentage of the total humus which was immediately soluble in ammonium hydroxide.	Milligrams of nitrogen in the ammonia retained from ammonium hydroxide by 10 grams of soil.[3]	Comparative amount of dilution in volume of the ammonium hydroxide extract of the Kingston soil to make it match in color similar extracts from the other soils.[4]	Lime (CaO) determined by the official method of the A.O.A.C.[5]	Lime (CaO) soluble in carbonated water.[6]	Soil materials too coarse to pass a sieve with holes ⅟₁₄ of an inch in diameter.
	Pounds.	Pounds.		Per cent.	Per cent.	Per cent.			Per cent.	Per cent.	Per cent.
Warren	27.2	32.9	21.0	2.67	0.90	33.71	21.21	3.3	0.382	0.029	7.00
Summit	47.4	92.9	96.0	1.73	0.84	48.55	19.61	4.0	0.386	*	22.30
Jamestown	75.8	152.7	101.5	0.85	0.53	62.35	10.41	5.0	0.261	*	1.15
Harrisville	151.5	207.3	102.8	1.46	0.42	28.77	14.09	6.6	0.429	0.036	11.75
Foster Center .	36.6	143.4	291.8	2.21	0.70	31.67	25.53	2.5	0.558	*	6.45
Niantic	9.9	43.4	338.4	0.95	0.46	48.42	7.92	4.0	0.112	*	14.65
So. Portsmouth	26.0	153.0	488.5	2.63	0.99	37.64	27.16	2.5	0.348	*	7.25
Hamilton	14.5	131.8	809.0	1.60	1.02	63.75	15.76	3.0	0.281	*	3.40
Kingston Hill .	6.6	161.4	2,345.5	5.15	1.99	38.64	36.09	0.0	0.412	*	*
Slocumville ...	1.0	101.8	10,080.0	5.08	1.41	27.76	43.77	0.3	0.553	*	1.10

* Not determined. [1] See method, p. 160. [2] See method, p. 163. [3] See method, p. 164. [4] See method, p. 164. [5] See method, p. 161. [6] See method, p. 157.

It will be seen that in the foregoing table the Warren soil which was least helped by lime, is placed at the top, the others being arranged in the order of the benefit noted, from top to bottom, with the Slocumville soil, representing a gain of 10,080 per cent. as a result of liming, placed at the foot of the list.

Comparing the percentages of material extracted immediately by treatment with ammonium hydroxide, with the gains from liming, it will be seen that there is no regular correspondence. The tests show a successive decrease in the first three soils while the crop increased. The Niantic soil shows a similar decrease. Of these soils, those at Niantic and Jamestown were exceedingly sandy, while those at Harrisville and Summit were quite gravelly. The result with the Warren soil was unexpectedly high. In the case of the balance of the "heavier" or more compact soils, a successive increase in humus immediately soluble in ammonium hydroxide was noticed, corresponding well, with the exception of the Slocumville soil, with the crop results. In fact this was the only method tried which indicated differences between the So. Portsmouth and Hamilton soils corresponding with those afforded by the crops. It will be noted that the Slocumville soil showed more benefit from liming than that at Kingston, though the latter gave a higher test by this method than the Slocumville soil. For the heavier classes of soils containing naturally considerable quantities of humus, this method gives much promise of usefulness. In the case of the more silicious soils containing but moderate amounts of humus, the method may perhaps indicate with considerable truthfulness the relative lime requirements within the particular class, but when it comes to comparisons of individuals of the one class with those of the other, it is possible that it fails to indicate the truth with sufficient accuracy on account of a considerable amount of the acidity being due more to inorganic, than to organic matter.

In support of this, it may be cited that many of our subsoils, which contain only minimum quantities of organic matter, are decidedly acid, indicating the presence of acid silicates, or other acid inorganic compounds. Mondesir[1] found that upon the destruction of all of the organic matter in a soil by means of "permanganate" at a temperature below 100° C., or by combus-

[1] *Compt. rend.*, 115, 317, August (1892).

tion at dull red heat, and after subsequent treatment at ordinary temperature with very dilute hydrochloric or nitric acid, followed by complete removal of these by washing with distilled water and subsequent heating for several hours at from 160° to 170° C., the soil residue was still acid. It decomposed calcium carbonate to some extent at ordinary temperature, and still further upon heating with water to the boiling-point.

It is of interest to note that in the case of the Slocumville soil, where beets almost absolutely refuse to grow without the aid of lime, only 27.76 per cent. of the total humus was immediately soluble in ammonium hydroxide, and in the Kingston soil which stood second in its degree of benefit from liming, but 38.64 per cent. was soluble or much less than in many of the soils where lime proved far less beneficial. The percentage of the total humus which is thus dissolved is not then in any sense a true measure of the lime requirement, though the absolute amounts of humus thus dissolved, have seemed, particularly in our quite heavy soils containing considerable total humus, to correspond with considerable accuracy to the tests with beets.

Though there seems to be no reason to think that there would be any relation between the lime requirement of soils and their total humus on soils of widely divergent character, yet upon soils of analogous mineral origin, it seemed probable that some such relation might exist. The results obtained when plotted in a curve, show, with a few exceptions, the same general trend as those obtained by direct extraction with ammonium hydroxide. In the case of the Jamestown and Harrisville soils the total humus was higher in the former while the amount of humus immediately extracted, was greater in the latter. In the Hamilton soil, the total humus runs too low to accord with the crop test, while the amount of humus immediately soluble in ammonium hydroxide is greater in the case of that soil than in the one at So. Portsmouth, or in agreement with the results secured with beets. In regard to the Kingston and Slocumville soils, the total humus is slightly less in the latter than in the former, but the results come far nearer agreeing with the crop test, than those obtained by immediate extraction of the humus.

In the case of the determination of the lime (calcium oxide) removable from the soil by digestion with hydrochloric acid, the

results are of marked interest, since they show in the most
striking manner that the data thus secured with our Rhode
Island soils furnished no reliable guide to their lime requirements.
As marked illustrations, it will be seen that the Foster Center
soil which contained 0.558 per cent. of calcium oxide, or the
greatest quantity of any of the soils examined, gave a gain in
crop of 291.8 per cent. as compared with a gain from liming of
only 21 per cent. in the Warren soil, which yielded only 0.382
per cent. of calcium oxide upon extraction with hydrochloric
acid.　Again the Slocumville soil showed by extraction with the
mineral acid 0.553 per cent. of calcium oxide, or but 0.005 per
cent. less than the Foster Center soil, and yet it was benefited
by lime more than any other soil tested giving a gain from its use
amounting to 10,080 · per cent.　The third highest content of
calcium oxide as determined by extraction with hydrochloric
acid was shown by the Kingston soil, which yielded 0.412 per
cent., and yet the only soil which showed a greater benefit from
liming was that at Slocumville where the percentage of calcium
oxide was even much higher than at Kingston.　These examples
are sufficient to show that even if by this method of analysis
considerable lime, even amounting to more than 0.5 per cent., is
shown to be present, it may nevertheless be in such combinations
that the soil will almost absolutely refuse to produce certain
crops until subjected to liming or other alkaline treatment.

The number of milligrams of nitrogen represented by the
ammonia retained by the soil, as determined by the method of
titration, accords better with the crop results in the case of the
Jamestown and Harrisville soils, than those obtained by
immediate extraction with ammonium hydroxide.　With the
Hamilton soil, the result by the latter method agreed more
closely with the crop tests, than those by the former, while in
the case of the Kingston and Slocumville soils, the agreement
with the crop results was more nearly perfect than those by any
other method employed.

Only two tests were made by treatment of the soil with
carbonated water.　The soil which was the more in need of
liming showed by this method a greater quantity of calcium
oxide removable by the treatment than the other, or just the
reverse of what should have been the case if the method were to

prove of value for the purpose in hand.   This fact, together with some experience in the same line in connection with other soils, coupled with the small quantities of calcium oxide removable, gave little reason to hope that the method was applicable for ascertaining the true lime requirements of our acid Rhode Island soils.

The tests by means of the comparison of the color of the ammonium hydroxide extract in the case of the four upper soils in the table, *viz.*, those from Warren, Summit, Jamestown, and Harrisville indicate a gradation in the opposite direction from those with beets.   The amount of total humus and the ammonia held by the soil as determined by the method of titration, agree, in the case of these soils, more nearly with the crop results. The results with the Foster Center and South Portsmouth soils, though not showing relative differences in the line of those exhibited by the crop, point, when compared with the first four soils in the series, in the same general way in relation to the soil requirements as the tests with beets.   The results with the South Portsmouth and Hamilton soils fail to accord between themselves with the beet test, though the result with the latter soil, when compared with the first four of the series, points in the right general direction.   Making a general comparison of the data secured with the Kingston and Slocumville soils with those in connection with the soils standing above them in the table, the tests point to the truth as concerns the needs of the soils.   Between themselves the tests would indicate a slightly greater need of lime in the Kingston soil than in the Slocumville soil, or just the opposite of the actual experience.

In closing this consideration of these results, it should be stated that it was recognized at the outstart that unfavorable physical conditions might exert a very disturbing influence, and that in consequence a method which takes into account only chemical defects could not be expected to agree in all cases with the crop results.   It was hoped, however, to combine physical analyses of the soil with the chemical, with the idea that possibly by a study of both, one might be helped very materially in arriving at a more correct judgment than by the use of either one singly. The resources at disposal have not as yet made it possible for these determinations to be made.   There seemed no reason to

conclude that a physical analysis of the soils only, could come as near revealing their lime requirements as chemical tests, particularly as it had already been abundantly demonstrated[1] that the beneficial action of lime upon our soils is, in a large degree, due to its correcting their prevailing acidity.

SUMMARY.

In consequence of the recognition of the acidity of many of the upland soils of Rhode Island and their consequent need of lime, it seemed desirable to find some chemical means for satisfactorily revealing their lime requirements, so as to avoid resorting to the slower and more expensive field experiments.

A number of methods have been tried, as follows :

(1) Moistening the soil with water, then bringing it in contact with blue litmus paper and noting with what rapidity and to what extent it reddens the paper as compared with some soil whose character is already well known. This method is highly effective in the hands of a close observer who has had much experience in testing soils of known character.

(2) Treatment of the soil with water to which a little ammonium hydroxide (ammonia water) has been added and noting whether, after settling, the liquid has assumed a dark brown or black appearance. This test applies only where the acidity is due in a considerable measure to acid organic substances. It may not apply in all sections of the country, as shown by Snyder, in Minnesota, but it has thus far proved a very useful and reliable test with Rhode Island and certain other New England and New York soils containing considerable quantities of humus. Gravimetrically applied this is the method of Müntz.

(3) The method employed by Holleman for determining the lime requirement of stiff clay soils in Holland, based upon the amount of lime (calcium oxide) removable by extracting with carbonated water. This method has given little promise of usefulness in testing our upland acid soils.

(4) The method of Tacke for determining the relative acidity of peat (moor) soils of North Germany based upon the amount of carbon dioxide which the acid ingredients of the soil can expel

[1] Eighth Annual Report, Rhode Island Agricultural Experiment Station, pp. 232–280 (1895); also Ninth Annual Report, pp. 294–318 (1896).

from calcium carbonate at ordinary temperatures in an atmosphere of hydrogen. This method has not seemed to be applicable to our acid upland soils.

(5) The determination of the total humus by a modification of the Grandeau method, which consists in removing the lime and magnesia from their combinations with the humus by treatment with dilute hydrochloric acid, and then dissolving the humus in ammonium hydroxide (ammonia water) and estimating the amount dissolved. In our granitic soils containing considerable quantities of humus, this method gives results standing in somewhat definite relation to the lime requirements.

(6) Determinations of the amount of lime (calcium oxide) which can be dissolved by weak hydrochloric acid by digestion at a high temperature for several hours (official method of the A. O. A. C.). This method furnishes no reliable basis for arriving at the lime requirement of our acid upland soils.

(7) Method by titration, based upon measuring the number of milligrams of nitrogen combined as ammonium salts and held by the soil when it is treated in a given way and for a given time with a very dilute solution of ammonium hydroxide.

The results by this method agree more closely with the crop tests than by any other method tried, though it is closely approximated to, by the gravimetric determination of the humus dissolved from the soil by extraction with ammonium hydroxide without the previous removal of the lime and magnesia.

(8) Method based upon the comparison of the color of the extract made from soils by treating directly with ammonia water, with the color of such an extract prepared from a like quantity of soil of known character. It seems probable that where the acidity is due largely to acid organic substances, this method may give fairly good results. The rapidity with which tests may be made by it is an important practical point in its favor as compared with the method as proposed by Müntz.

(9) Method based upon the amount of carbon dioxide expelled by a given amount of soil from calcium carbonate when the two are heated together at the boiling-point in the presence of water. This method gives promise of much value if the period of heating is made uniform and very brief, and if the carbon dioxide liberated is easily and accurately determined. Routine work

has thus far prevented further attempts to carry out a satisfactory study of this method including the perfection of its details.

LABORATORY OF THE RHODE ISLAND
AGRICULTURAL EXPERIMENT STATION.

NEW BOOKS.

ANALYSIS OF WHITE PAINTS. A Collection of Notes on the Chemical Analysis of White and Tinted Paints. BY GEORGE H. ELLIS, B.SC. Evanston, Ills.: The Technical Press. 8vo. pp. 57.

The notes under review were originally published in the *Paint, Oil and Drug Review*, of Chicago, and were prepared and edited by one who has had long practical experience in the technical examination of the products treated. They consist really of a collection of methods for analysis of paints and pigments long used by the author in his daily practice largely devoted to the products of the paint industry, and as the methods have been thoroughly tested and are-described in the fullest detail they will be particularly useful to those chemists whose work has given them but limited practice with such products and methods.

With the methods of analysis in each case are presented results obtained by the author in the use of the methods, showing the average composition of the commercial product treated, and thus offers much useful information not easily found elsewhere. The book is commended to those whose duties lead them occasionally in the lines of work here treated and indeed to all needing guidance in the technical examination of pigments and paints.

WM. McMURTRIE.

THE CHEMISTRY OF SOILS AND FERTILIZERS. BY HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Agricultural Experiment Station. Easton, Pa.: The Chemical Publishing Co. 1899. 12 mo. ix + 277 pp. Price $1.50.

We are told in the preface that this book was intended primarily to be used as a text-book in the author's classes. This fact explains the "experiments" and "review questions" which are given at the end of the book, as well as the condensed manner in which it is written.

It should answer admirably the purpose for which it was intended. The subject-matter is well chosen, well arranged, and clearly and concisely stated.

The style is as nearly popular as is possible with applied chemistry, and the book will be found of value even to agriculturists whose education has not included a course in chemistry.

W. D. BIGELOW.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. BY ARTHUR H. ELLIOTT, Ph.D. and GEORGE A. FERGUSON, Ph.B. Third edition, revised and enlarged. New York: Published by the Authors. 155 pp. Price, $1.50.

This manual contains a straightforward, carefully detailed procedure for the systematic qualitative examination of solutions or substances of moderate complexity. The analytical scheme is accompanied by a series of "solution tests" which the student is required to apply to each metal or acid radical and which include the reactions with certain general reagents, and with such special reagents as yield typical products. In connection with these tests a useful list of the important commercial compounds of each metal is given.

Certain of the schemes for the separation of the metals used in former editions have been altered or replaced by others (notably those of the copper and barium groups), and the procedure for the separation and detection of the acid radicals has been enlarged and improved. The book is liberally provided with tabulated statements of the methods of separation, and of the results of the "solution tests." The student can, indeed, hardly go astray within the field covered by the manual, so minute are its directions; yet, under the conditions imposed, the instructor will need to use much effort to encourage independence of thought and action on the part of the student.

The introduction of the "solution tests" is, perhaps, no more a proper subject for criticism in this manual than in many other similar works, but it may fairly be questioned whether so many of these isolated tests do not, by interrupting the study of the systematic plan of analysis, by confusing the beginner and lessening his interest, fail to serve a really useful purpose when the teaching of qualitative analysis is the central aim. To those teachers, however, who favor this method of presentation, the book will appeal strongly as a guide for beginners.

H. P. TALBOT.

PRACTICAL METHODS FOR DETERMINING MOLECULAR WEIGHTS. BY HENRY BILTZ, Privatdocent at the University in Greifswald. Translated by HARRY C. JONES and STEPHEN H. KING. Easton, Pa.: The Chemical Publishing Company. 1899. 235 pp. Price, $2.00.

Previous to the appearance of the German edition of this work there was no satisfactory reference book on the determination of molecular weights, particularly by the vapor-density methods. Windisch's '' Die Bestimmung des Moleculargewichts '' was so voluminous and contained so many processes, with so much descriptive matter that it required an experienced hand to find just what was wanted, and therefore could not be used as a satisfactory laboratory guide. Fuchs's '' Anleitung zur Molecular-gewichts Bestimmung'' was entirely satisfactory, but unfortunately was confined to the cryoscopic processes, thus leaving no satisfactory laboratory guide for the vapor-density methods.

This translation places in the hands of English-reading students a masterly summation of the practical methods for determining molecular weights by the vapor-density and the cryoscopic methods, with a careful criticism of the different procedures, and a comparison of the usefulness of one with the other. The author has been strongly under the influence of Victor Meyer, which gives an authoritative value to the Meyer displacement method and its various modifications. The separate methods are described with clearness and with that close attention to essential details which clearly shows the result of much experience. The critical discussion of the results obtained by the various methods is extremely valuable, especially those values obtained from substances which dissociate on heating, and those which suffer electrolytic dissociation in solution. The references to the literature are frequent and form a valuable part of the book.

The book contains chapters on the vapor-density methods of Meyer, Dumas, Gay-Lussac, and Hofmann, with the various modifications; and on the methods for determining molecular weights of substances in solution by the rise in boiling-point and the lowering of the freezing-point. The method of Nernst based on the principle of the lowering of the solubility is treated briefly. The process worked out by Traube and based on a comparison of the values from a determination of the molecular

volume and the theoretical value, is described, but is not recommended.

The translators have done their work satisfactorily. They have added a short chapter on the method and apparatus devised by Jones for the determination of molecular weights by the rise in boiling-point.   HENRY FAY.

THE COST OF LIVING AS MODIFIED BY SANITARY SCIENCE. BY·ELLEN H. RICHARDS. 121 pp. New York: John Wiley & Sons. 1899.

This little book is a great disappointment to the student of sanitary science because of the misleading title which it bears. In no single instance has the author given us an idea whether the cost of living has been modified either favorably or unfavorably by sanitary science. She has shown that the cost of living has been increased by various causes which must, however, be classed as economic, social, and industrial.

The principal causes to which she attributes the increased cost of living are: The gross waste on the part of the housewife in reckless and useless expenditure for commodities which are unessential to health and happiness, and the improper utilization and even waste of the commodities purchased; also, the lack of proper interest in her duties, and want of appreciation of the importance of those duties on the part of the housewife. The factors which have brought about the foregoing conditions are mainly industrial, due to the removal of all manufacturing from the home to the factory, changing the occupation of the housewife almost altogether from that of a producer to that of a distributor. It will be seen that none of these causes are traceable to sanitary science.

The subject-matter presented is of marked interest and of the highest importance, and it is unfortunate therefore that it has been presented under a misleading title. Moreover it is to be regretted that the author has not adhered to the title given to the book because there is every reason to believe that the cost of living has been modified by sanitary science and a contribution embodying this information would be most valuable.

                                   D. H. BERGEY.

THE JOURNAL

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ON THE ACTION OF CERTAIN ACID REAGENTS ON THE SUBSTITUT~D UREAS.

[FIRST PAPER.]

BY F. B. DAINS.

Received March 14, 1900.

IN the course of an investigation on the isourea ethers,[1] the question arose regarding the anilido hydrogen as to its ease of replacement by, a· l its reactivity toward, acid reagents. Since the amount of experimental evidence concerning the action of acids and acid chlorides on the substituted ureas is relatively small, a study is being made of the behavior of these bodies toward such reagents.

With an easily replaceable hydrogen, a very interesting synthesis would be possible: namely, the direct formation of acyl thio and oxygen ureas of the general type:

$$\begin{array}{c} RNH \\ \diagdown \\ \diagup \\ RN \end{array} CO(S).$$

$$\diagdown \\ COR$$

When, however, acyl chlorides, acid anhydrides, and acids act upon these ureas, while it seems probable in many cases that the

[1] This Journal, 21, 181.

anilido hydrogen is the first point of attack, with the interme-
diate formation of an acyl derivative, only under especial circum-
stances have these intermediate bodies been isolated when this
method of preparation is used.   For instance, the oxygen deriv-

atives $\begin{array}{c} \text{RNH} \\ \diagdown \\ \diagup \\ \text{RN} \end{array} \text{CO}$ have never been prepared directly, but only by

$\begin{array}{c} \diagdown \\ \text{COR} \end{array}$

(1) the addition of acetanilide to phenyl isocyanate,[1]
(2) the action of acid chlorides on the isourea ethers.[2]

The corresponding sulphur body $\begin{array}{c} \text{RNH} \\ \diagdown \\ \diagup \\ \text{RN} \end{array} \text{CS}$ has, however, been

$\begin{array}{c} \diagdown \\ \text{COR} \end{array}$

isolated in the following cases:

(1) Werner[3] heated dibenzyl thiourea and acetic anhydride
to the boiling-point of the latter, and obtained acetyl dibenzyl
thiourea, besides small quantities of benzyl mustard oil and
benzyl acetamide, the usual products of the reaction.   Werner
thinks that with fatty thioureas such an acyl derivative is usually
formed, but he only succeeded in isolating it in the above
instance.

(2) Deninger has found that acetyl chloride and thiocarban-
ilide in pyridine solution give mono acetyl thiocarbanilide.[4]

(3) Recently Hugershoff,[5] by modifying the process used by
Werner, and heating the mixture of thiocarbanilide and acetic
anhydride only to the temperature of a boiling water bath, suc-
ceeded in isolating acetyl thiocarbanilide.   A yield of 45 per
cent. was obtained, the rest of the thiocarbanilide having formed
mustard oil and acetanilide, the products obtained by Werner at
the temperature of boiling acetic anhydride.

These acyl ureas are relatively unstable bodies, and readily
dissociate above their melting-points into the corresponding cya-

[1] McCreath : *Ber. d. chem. Ges.*, **8**, 1181.
[2] Dains : This Journal, **21**, 182.
[3] *J. Chem. Soc.*, **50**, 406.
[4] *Ber. d. chem. Ges.*, **28**, 1322.
[5] *Ibid.* (1899), 3649.

nates and anilides, thus giving opportunity for secondary reactions.

While it seems extremely probable, and in a number of cases is definitely proved, that the acid chlorides and anhydrides react with the ureas with the formation of such intermediate acyl ureas, yet under the conditions of the experimental work in this paper, the temperature required to produce reaction was so high that such acyl ureas were never isolated, but only their decomposition products. This fact has given rise to some interesting results.

The work in this paper has been confined to a study of the action of acids and acid chlorides on such ureas as carbanilide and thiocarbanilide, the only exception being some experiments on the action of acetic anhydride and the above reagents on the oxygen and sulphur isourea ethers. The interaction between these reagents and the monosubstituted and acyl ureas will be discussed in a later paper.

<div align="center">EXPERIMENTAL.</div>

Organic Acids and Carbanilide.—Werner[1] has shown that pure acetic acid decomposes diphenyl urea at $160°-170°$, giving acetanilide, carbon dioxide, and water.

Organic Acids and Thioureas.—Cain and Cohen, while investigating the " action of acetic acid on phenyl thiocarbamide," heated absolute acetic acid and thiocarbanilide at $130°-140°$ for three to four hours. They simply state that diphenyl urea was one of the products.[2] This is wholly in accord with the general action of anhydrous acids at temperatures above $130°$. At a lower temperature, somewhat different results are obtained. Thus 9 grams of thiocarbanilide and 20 cc. of pure acetic acid were heated in a water-bath for thirty hours. The residual solid, when filtered off and examined, proved to be thiocarbanilide, and not diphenyl urea. On distilling the acid filtrate with steam, phenyl mustard oil came over, while the distilling flask was found to contain acetanilide and a base that melted at $145°$,— its picrate melted at $180°$, and was, therefore, triphenyl guanidine. The picrate of pure triphenyl guanidine was found by

[1] *J. Chem. Soc.*, **59**, 550.

[2] Cain and Cohen : *J. Chem. Soc.*, **59**, 328.

experiment to melt at 180°, and not at 178°, as given in the literature.

Under these conditions, then, the reaction follows out the lines of the decomposition of the thiocarbanilides with aqueous hydrochloric acid, the difference centering in the fact that the products of the reaction tend to form anilides with the organic acid present,—a tendency more apparent when higher temperatures are used. In this case there is first dissociation into phenyl mustard oil and aniline; and as secondary reactions, the formation of acetanilide from the aniline and the glacial acetic acid, and also, though more slowly, from the acid and the mustard oil. This interpretation is confirmed by the fact that, while at the above temperature no carbanilide is formed when absolute acid is used, with aqueous acid diphenyl urea is produced (as shown by experiment). This, as the investigation of Werner shows, is due to the action of the aqueous acid upon the phenyl thiocarbamide. It was found by direct experiment that the final products of 75 per cent. acetic acid, and thiocarbanilide at water-bath temperature are acetanilide and diphenyl urea, although the odor shows that mustard oil is an intermediate product.

Butyric Acid and Thiocarbanilide.—2.3 grams of thiocarbanilide and 2 grams of butyric acid were heated at 140°–160° for two hours. Reaction set in with the evolution of carbon dioxide and hydrogen sulphide. From the residue, by crystallization from alcohol, there was isolated butyric anilide and diphenyl urea. Carbon oxysulphide was probably evolved, but no effort was made to detect it in the presence of hydrogen sulphide and carbon dioxide. In all of these experiments, it may be said, traces of the free amine could be detected.

Benzoic Acid and Thiourea.—Molecular quantities of benzoic acid and diphenyl thiourea, at 160°–180°, evolve hydrogen sulphide, carbon dioxide, and water. As the formation of gas ceases, the melt becomes semisolid, and on examination is found to consist of a little benzoic acid which was extracted with dilute alkali, benzanilide, and a small amount of diphenyl urea.

Diparatolyl thiourea and benzoic acid, under like conditions, gave as gaseous products carbon dioxide and hydrogen sulphide, and a residue of *p*-benztoluid *p*-carbtoluid, and a little benzoic acid.

Salicylic Acid and Diphenyl Thiourea.—A mixture of these bodies in molecular proportions, when heated, liquefied at 140°, and at 150° slowly gave carbon dioxide and hydrogen sulphide. Caustic alkali separated the melt into two portions : one soluble in alkali, the other insoluble. This latter proved to be diphenyl urea. The portion soluble in the caustic soda consisted of salicylic anilide (m. p. 133.5°) and a little salicylic acid. Besides these products traces of aniline and phenol were formed,—the latter doubtless due to a slight decomposition of the salicylic acid.

The experiments presented show that the reaction between the thioureas and organic acids of the type RCOOH, proceeds along fairly definite lines. The products to be accounted for are carbon dioxide, hydrogen sulphide, water, the anilide, mustard oil and carbanilide.

The main reaction is the one already indicated :

$$\text{I.} \quad \underset{\text{RNH}}{\overset{\text{RNH}}{>}}\text{CS} + \text{RCOOH} = \text{RNCS} + \text{RNH}_2.\text{RCOOH}.$$
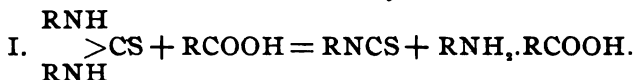
At the temperature of the reaction the amine and the acid unite.

$$\text{II. } \text{RCOOH} + \text{RNH}_2 = \text{RNHCOR} + \text{H}_2\text{O}.$$
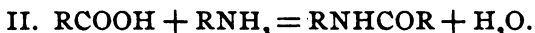
At the same time the mustard oil is attacked.

$$\text{III. } \text{RNCS} + \text{RCOOH} = \text{RNHCOR} + \text{COS.} \quad (\text{HOH} + \text{COS} = \text{CO}_2 + \text{H}_2\text{S.})$$
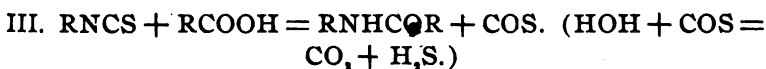
Only the carbanilide remains to be accounted for. This body, it will be remembered, is produced only when high temperatures are used in the reaction between thiocarbanilide and anhydrous acids. At the water-bath temperature none was formed. Werner, who has studied the reaction between acetic acid and phenyl mustard oil, says that the decomposition occurs according to the following equation :[1]

$$2\text{RNCS} + 3\text{H}_2\text{O} = (\text{RNH})_2\text{CO} + 2\text{H}_2\text{S} + \text{CO}_2.$$

In view of this it might be said that the carbanilide is due to the water formed in the reaction and the mustard oil set free at the same time. But such a conclusion must be erroneous for the following reasons :

a. At water-bath temperature none is formed ;

[1] *J. Chem. Soc.*, **59**, 545.

b. Much, if not all, of the water escapes at the temperature of the reaction;

c. More carbanilide is often produced than the above equation accounts for.

A very probable hypothesis is the following: at the high temperature employed, there is more or less dissociation of the thiocarbanilide into carbodiimide and hydrogen sulphide.

The carbodiimide thereupon reacts with the organic acid as follows:[1]

$$(RN)_2C + 2RCOOH = (RNH)_2CO + (RCO)_2O.$$
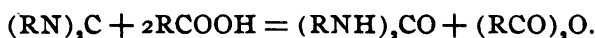
Dibasic Acids and the Thioureas.—Diphenyl thiourea and oxalic acid were heated at $160°-170°$. The mixture melted readily, decomposed with the evolution of gas, and then partially solidified.

The gaseous products consisted mainly of carbon dioxide and hydrogen sulphide. From the solid residue, hot alcohol extracted traces of phenyl mustard oil and a little unchanged thiourea. The insoluble portion proved to be oxanilide (m. p. 240). The main reaction, then, is as follows:

$$\begin{matrix} RNH \\ \diagdown \\ \diagup \\ RNH \end{matrix} CS + \begin{matrix} HOCO \\ | \\ HOCO \end{matrix} = CO_2 + H_2S + \begin{matrix} CONHR \\ | \\ CONHR \end{matrix}$$
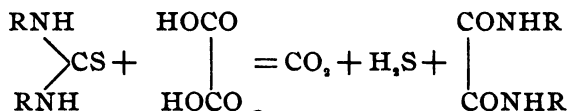
Traces of aniline could also be detected, probably in the form of aniline oxalate. No oxanilide was discovered.

Thiocarbanilide (11 grams) and succinic acid (5 grams) require a temperature of $170°$ before reaction sets in. At this point, however, much carbon dioxide, hydrogen sulphide, and water are evolved. The other products consisted of small amounts of aniline and mustard oil, while the residual solid could be separated by fractional crystallization into succinanil and succinanilide.

The main results can be expressed as follows:—

$$I. \quad \begin{matrix} RNH \\ \diagdown \\ \diagup \\ RNH \end{matrix} CS + 2 \begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} = 2 \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \diagup \diagdown NR + 2H_2O + H_2S.$$

[1] Dains: This Journal, **21**, 157.

II. $\begin{matrix} RNH \\ \diagdown \\ CS+ \\ \diagup \\ RNH \end{matrix}$ $\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix}$ $=$ $\begin{matrix} CH_2CONRH \\ | \\ CH_2CONRH \end{matrix}$ $+H_2O+CO_2+H_2S.$
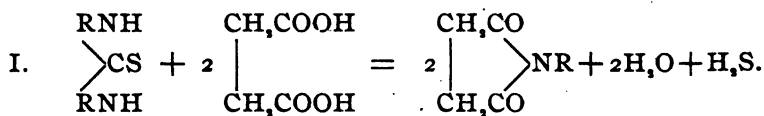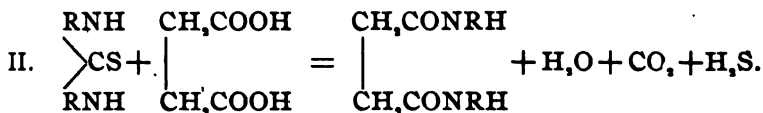
These reactions are almost identical with those that occur when the anhydride is used instead of the acid. For instance, Dunlap[1] has found that succinic anhydride and thiocarbanilide give succinanil, succinanilide, carbonyl sulphide, and aniline. My own experiments confirm these results and show that with the elevation of temperature, there is increase in the amount of succinanilide formed. Thus, equal molecules of di-*p*-tolyl thiourea and succinic anhydride, when heated at 160°–180°, give as gaseous products carbon dioxide, hydrogen sulphide, water, and COS. The residue consisted of *p*-tolylsuccinimid and *p*-succintoluid.

It is possible that formation of succinic anhydride precedes the interaction with the thiocarbanilide, as seems to be the case with phthalic acid.

Thiocarbanilide and phthalic acid (equal molecules) reacted at 170°, with the evolution of hydrogen sulphide and carbon dioxide.

The residue was washed with cold alcohol: this removed, as was found, phenyl mustard oil, a little aniline, and a solid melting at 125°–130° which proved to be phthalic anhydride. The main product, which was insoluble in the cold alcohol, proved to be phthalanil (m. p. 205°). The reaction proceeds as if the anhydride had been used instead of the acid. The results again are in accordance with the experiments of Dunlap[1] who found that thiocarbanilide and phthalic anhydride react at 170° with the formation of phthalanil and mustard oil.

Before this paper of Dunlap's was seen, experiment showed that *p*-tolyl thiourea and phthalic anhydride react easily and smoothly at 160° yielding COS, traces of water and hydrogen sulphide, and practically quantitative amounts of p-tolyl mustard oil and *p*-tolyl phthalanil. An excess of the acid or acid anhydride increases the yield of phthalanil and decreases that of the mustard oil, since it was found by experiment that equal mole-

[1] *Am Chem. J.*, **18**, 332.

cules of phthalic anhydride and mustard oil at 160° slowly give COS and phthalanil. On the contrary phenyl mustard oil and succinic anhydride do not react at 180°, but when boiled together tar is produced and an odor of phenyl isocyanate developed.

$$\begin{matrix} RNH \\ \quad \\ RNH \end{matrix} CS + C_6H_4 \begin{matrix} COOH \\ \quad \\ COOH \end{matrix} = C_6H_4 \begin{matrix} CO \\ \quad \\ CO \end{matrix} NR + RNCS + 2H_2O.$$
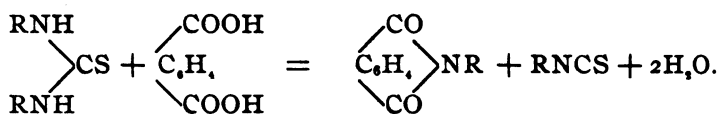
Acid Chlorides and Ureas.—When acid reagents' like the acid anhydrides and the acid chlorides act upon the disubstituted ureas, the anilido hydrogen seems to be the main point of attack, although the actual mechanism of the reaction, whether it be one of addition or direct replacement of the hydrogen, cannot as yet be settled experimentally. The evidence points, however, to the intermediate formation in some way of an acyl derivative.

With the oxygen ureas such a compound, $\begin{matrix} RNH \\ \quad \\ RN \\ \quad \\ COR \end{matrix} CO$, can

never be obtained by the direct action of the acid chloride since the acyl body decomposes at a temperature below that at which the reaction is carried out.

The equations evolved in the interaction of an acid chloride and carbanilide can be represented as follows :

I. $(RNH)_2CO + RCOCl = RNHCONR + HCl =$
$$\underset{COR}{|}$$
$$RNHCOR + RNCO + HCl.$$
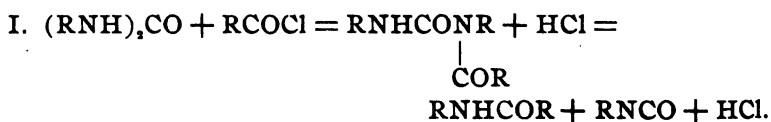
Under the conditions of the experiment, the acyldialphyl urea breaks down into an anilide and isocyanate, which in turn react, giving carbon dioxide and an amidine derivative.

II. $RNHCOR + RNCO + HCl = RNH—CR.HCl + CO_2.$
$$\underset{RN}{\diagup\!\!\diagup}$$
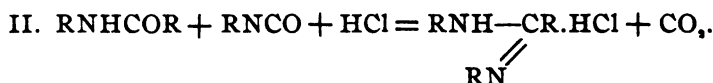
Diphenyl urea was heated with a slight excess over 1 molecule of acetyl chloride in a sealed tube for three hours at 150°. The tube opened with pressure due to carbon dioxide and a little

hydrochloric acid. After the addition of water the reaction-product was shaken out with ether. This removed acetanilide.

On treating the water solution with an alkali, a base was precipitated which, on examination, was found to be acetdiphenylamidine, m. p. 131°–132° (α-phenylimido-α-phenylamidoethane). This base can be purified by recrystallization from alcohol or by dissolving in benzene, passing in hydrogen chloride, and then extracting the pure hydrochloride with water. This removes gummy impurities that are apt to remain persistently with the base. It was further identified by its platinum salt, which melted at 210°.

Analysis of two separate preparations :

1. 0.1810 gram substance gave 0.0430 gram platinum.
2. 0.1400 gram substance gave 0.0326 gram platinum.

	Calculated for $(C_{14}H_{14}N_2)_2H_2Pt.Cl_6$.	Found.	
		1.	2.
Platinum ·············	23.47	23.75	23.30

The picrate of this base melts at 165°.

I. $(C_6H_5NH)_2CO + CH_3COCl =$

$$C_6H_5NHCOCH_3 + C_6H_5NCO + HCl.$$

II.
$$\begin{array}{c} C_6H_5NH \\ \diagdown \\ \diagup \\ C_6H_5N \end{array}\!\!\!C.CH_3.HCl + CO_2.$$
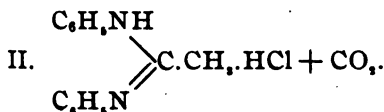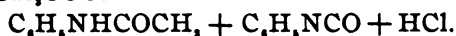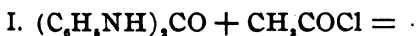
Nine grams carbanilide and 5 cc. butyryl chloride were heated at 150°–170° for four hours. The tube opened with much pressure due to carbon dioxide and hydrogen chloride. The contents, which formed an oily mass filled with bubbles of gas, were dissolved in alcohol and the alcohol evaporated to remove excess of the acid chloride. The ether extract gave 0.5 gram of butyric anilide, which crystallized from ligroin in square plates.

The water solution was found to contain a base, α-diphenyl butane amidine, C_3H_7—C$\diagup^{NC_6H_5}_{\diagdown NHC_6H_5}$ [Diphenyl butyryl amidine.] This crystallizes from alcohol, in which it is very soluble, in fine star clumps of needles, which melt at 105°.
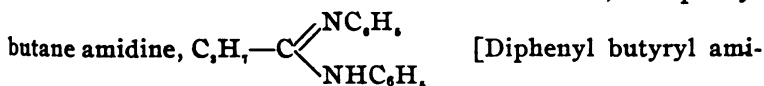
Analysis resulted as follows :

0.600 gram substance (Kjeldahl) required 4.9 cc. normal acid.

<div style="text-align:center">Calculated for
$C_{16}H_{18}N_2$.   Found.</div>

Nitrogen................ 11.78   11.46

When a solution of the amidine hydrochloride and chlorplatinic acid is allowed to evaporate slowly, a red platinum salt is produced.·

Analysis gave the following :

0.3780 gram salt gave 0.0832 gram platinum.

<div style="text-align:center">Calculated for
$C_{32}H_{28}N_2Pt.Cl_6$.   Found.</div>

Platinum 21.98   22.01

Molecular proportions of carbanilide and benzoyl chloride were heated at 160°–170° for four hours. As before, carbon dioxide was formed. From the solid contents of the tube, benzene ·extracted benzanilide, m. p. 161°. The residue insoluble in benzene dissolved readily in water and proved to be the hydrochloride of a base, diphenyl benzenyl amidine, formed by the action of the phenyl isocyanate on the benzanilide.

Thus Kuhn[1] has shown that phenyl isocyanate and benzanilide react at 180°–200° to form the above amidine and carbon dioxide. The base that melted at 145° was further identified by its platinum salt. This melted at 212° and gave the following figures on analysis :

0.1892 gram substance gave 0.0382 gram platinum.

<div style="text-align:center">Calculated for
$C_{26}H_{24}N_4PtCl_6$.   Found.</div>

Platinum................ 20.39   20.19

When molecular proportions of benzoyl chloride and carbanilide are heated in an open flask at 160°–200°, carbon dioxide and hydrochloric acid are given off and the intermediate formation of phenyl isocyanate is very apparent from the odor. Diphenyl benzenyl amidine was isolated as before and was identified by its own melting-point and that of its picrate (m. p. 216°).

Acyl Chlorides and Dialphyl Thioureas.—Reagents of this class act more readily on the thioureas than on the corresponding oxygen derivatives. The products of the reaction are largely dependent upon the following conditions : the presence of a solvent such as pyridine, the temperature, and the fact that the mustard oils

[1] *Ber. d. chem. Ges.*, 18, 1476.

are less reactive than the corresponding isocyanates, and so do not tend to react with the anilide formed.

Deninger[1] has shown that by dissolving thiocarbanilide in pyridine, acyl chlorides attack the anilido hydrogen with great ease at ordinary temperatures, forming a stable substitution product. For instance, acetyl chloride and thiocarbanilide, under these conditions, give acetyl thiocarbanilide.

$$\begin{matrix} C_6H_5NH \\ \diagdown \\ C_6H_5NH \diagdown \end{matrix} \!\! \begin{matrix} \diagup CS \\ \diagdown COCH_3 \end{matrix}$$
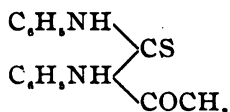
With benzoyl chloride and diphenyl thiourea, a dibenzoyl derivative was obtained. Like the oxygen bodies of similar constitution, these acyl thiocarbanilides are easily decomposed. Thus, acetyl thiocarbanilide, when heated above its melting-point or when boiled with water, gives phenyl mustard oil and acetanilide, which two components show no tendency to unite again even when heated. On the other hand, phenyl isocyanate and acetanilide heated in a sealed tube to 150° unite to form acetyl diphenyl urea.[2]

In the absence of pyridine, which combines with the hydrochloric acid set free, my experiments show that heat is required to effect complete reaction between the acyl chloride and the thioureas, and that under these conditions no intermediate product corresponding to the acyl thiocarbanilide can be isolated.

The general reaction between an acyl chloride and a dialphyl thiourea can be expressed as follows :

$$\begin{matrix} RNH \\ \diagdown \\ RNH \end{matrix} CS + RCOCl = \begin{matrix} RNH \\ \diagdown \\ RNCOR \end{matrix} CS + HCl = RNCS + RNHCOR$$
$$+ HCl.$$
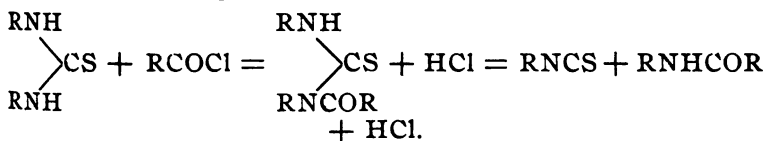
Mustard oil and an acyl anilide are the main products, while occasionally small quantities of an amidine base are formed.

$$RNCS + RNHCOR = \begin{matrix} RNH \\ \diagdown \\ RN \end{matrix} CR + COS.$$
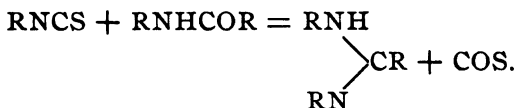
[1] *Ber. d. chem. Ges.*, **28**, 1332.
[2] McCreath : *Ibid.*, **8**, 1181.

Acetyl Chloride and Thiocarbanilide.—Diphenyl thiourea was treated with a slight excess over 1 molecule of acetyl chloride, and, as no reaction occurred at ordinary temperatures, the mixture was warmed to 50° on the water-bath, until the evolution of hydrochloric acid ceased. The oily product, which became semisolid on cooling, was distilled with steam. Phenyl mustard oil came over. This was identified by its properties, and the formation of monophenyl thiourea. On concentrating the water solution of the residue not volatile with steam, acetanilide (m. p. 114°) was obtained. The filtrate from this, when neutralized with alkali, gave small quantities of a base which proved to be acetdiphenyl amidine, a product formed in much larger quantities in the reaction between acetyl chloride and carbanilide, and identical with the body thus obtained.

Butyryl chloride and diphenyl thiourea react with ease, giving much hydrochloric acid, and an oily product from which can be isolated phenyl mustard oil and butyric anilide. Small amounts of an impure base are also formed.

When molecular quantities of benzoyl chloride and thiocarbanilide are heated to 150°, reaction ensues with the evolution of hydrogen chloride, a little carbon dioxide, and a gas that blackens lead acetate paper. On distilling the product with steam, or by separating with cold alcohol, there can be isolated almost quantitatively phenyl mustard oil and benzanilide. Traces of the base diphenylbenzenyl amidine are also formed.

Di-*m*-xylyl thiourea and benzoyl chloride, under like conditions, react at 120°. The products were the benzoyl derivative of metaxylidine ($CH_3CH_3NH_2,1,3,4$ (m. p. 192°), and xylyl mustard oil, which, with alcoholic ammonia, gave the monothiourea (m. p. 175°). Traces of an impure base were also formed.

Greater elevation of temperature does not favor this reaction between the acid chlorides and the thioureas. For instance, molecular quantities of benzoyl chloride and di-*o*-tolyl thiourea were heated in a sealed tube at 180°–200°. The tube opened with slight pressure, and the issuing gas burned with a pale blue flame. The contents of the tube consisted of *o*-tolyl mustard oil, *o*-benztoluide, much tar, and a small amount of an impure base.

Allylphenyl thiourea was warmed on the water-bath with a slight excess of acetyl chloride. The reaction-product formed a

thick oil, with the evolution of a little hydrogen chloride.   On distilling this oil with steam, a few drops only of phenyl mustard oil were obtained, and the residue in the distilling flask, with the exception of a little tar, was completely soluble in water. From this, alkali threw down a base which, without further purification, melted at $115°$ and gave a picrate (m. p. $153°$).   It was, therefore, N-phenyl propylene pseudo thiourea. (2-Phenyl amido-5-methyl-4,5-dihydrothiazol.)   This was further established by the analysis of the platinum salt.

0.6003 gram substance gave 0.1477 gram platinum.

	Calculated for $(C_{10}H_{12}N_2S)_2H_2PtCl_6$.	Found.
Platinum	24.53	24.60

The acyl chloride evidently causes a practically quantitative rearrangement.   Boiling with hydrochloric acid brings about the same change.[1]

The Action of Acid Reagents on Isourea Ethers.—A study begun in a former paper on the action of acids, acid chlorides, and acid anhydrides on the isourea ethers is here continued and extended to the corresponding sulphur ethers.

Organic acids act with great ease upon the isourea ethers. Thus ethylisodi-*o*-tolyl urea and glacial acetic acid give ethyl acetate and carbanilide, as has been shown in a former paper.[2]

Towards acids and acid reagents the thio ethers show remarkable stability.   Ethyl isothiocarbanilide can be boiled with glacial acetic acid without effect, the original base being recovered unchanged.   When heated at $180°$ with acetic acid the tube opens with pressure ; the issuing gases burn and form a white precipitate with a silver nitrate solution.   The solid residue consists of pure acetanilide.   The odor of mercaptan is apparent.

Acid of Acetic Anhydride upon the Oxygen Urea Ethers.—Ten grams of amylisodi-*o*-tolylurea and 3.5 grams of acetic anhydride were mixed.   Since no apparent reaction took place after standing at ordinary temperatures, the solution was heated in an oil-bath at $150°-160°$ for one and one-half hours.   The product, which remained oily after twelve hours' standing, was distilled at 12 mm. pressure ; there was isolated amyl acetate, a

[1] Prager: *Ber. d. chem. Ges.*, **22**, 2991.
[2] This Journal, **21**, 170.

little unchanged acetic anhydride, *o*-acettoluide, and a trace of *o*-ditolylurea. The latter may be due to traces of moisture or of acetic acid in the anhydride.

Equal molecules of ethyl isocarbanilide and of acetic anhydride were heated in a test-tube fitted with an air-condenser and a calcium chloride tube for eight hours at 160°–170°. Ethyl acetate was detected by its odor. The oily product was treated with alcohol to get rid of the excess of the acetic anhydride and then recrystallized from water. Acetanilide was isolated. This same reaction was found to take place with equal ease at 130°–140°. At this latter temperature methylisocarbtoluide and acetic anhydride give methyl acetate and *o*-acettoluide. The yield of acetanilide or of *o*-acettoluide seems to be quantitative.

As in all reactions with acidic reagents there is doubtless first addition to the double bond with the formation of an unstable addition-product.

$$\text{I.} \quad \begin{matrix} \text{RNH} \\ \diagdown \\ \diagup \\ \text{RN} \end{matrix}\!\!\!\text{COC}_2\text{H}_5 + (\text{CH}_3\text{CO})_2\text{O} \longrightarrow \begin{matrix} \text{RNH} \\ \diagdown \\ \diagup \\ \text{RN} \end{matrix}\!\!\!\text{C}\!\!\!\begin{matrix} \text{OC}_2\text{H}_5 \\ \diagup \\ \diagdown \\ \text{OCOCH}_3 \end{matrix} \longrightarrow$$

$$\begin{matrix} \text{COCH} \end{matrix}$$

$$\begin{matrix} \text{RNH} \\ \diagdown \\ \diagup \\ \text{RN} \end{matrix}\!\!\!\text{CO} + \text{CH}_3\text{COOC}_2\text{H}_5.$$

$$\begin{matrix} \text{COCH} \end{matrix}$$

$$\text{II. } (a) \quad \begin{matrix} \text{RNH} \\ \diagdown \\ \diagup \\ \text{RN} \end{matrix}\!\!\!\text{CO} \longrightarrow \text{RNHCOCH}_3 + \text{RNCO.}$$

$$\begin{matrix} \text{COCH}_3 \end{matrix}$$

(*b*) $\text{RNCO} + \text{O(COCH}_3)_2 \longrightarrow \text{RN(COCH}_3)_2 + \text{CO}_2.$
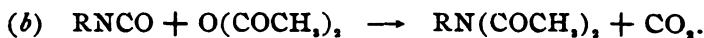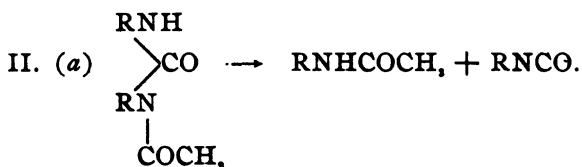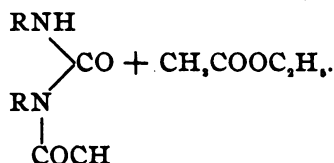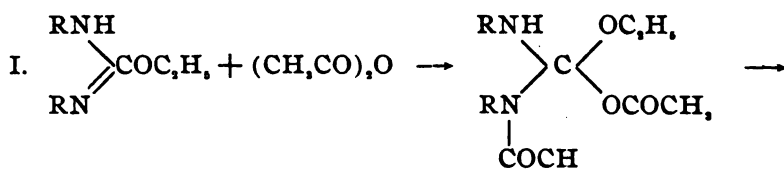
At the temperature of the experiments, 130°–140°, not only is this intermediate addition-product broken down, but the acetyl diphenyl urea formed is dissociated into phenyl cyanate and acetanilide: and the phenyl cyanate in turn reacts with the excess of acetic anhydride to form diacetanilide. That the diacetani-

lide was not isolated is not surprising, since it is very easily saponified.[1]

The experimental evidence for equation II is as follows :

(a) Acetyl diphenyl urea, when heated a little above its melting-point, dissociates, giving phenyl isocyanate and acetanilide.

(b) Acetyl diphenyl urea, when heated with acetic anhydride at 130° for two hours, and the resulting product recrystallized from water, gives a quantitative yield of acetanilide.[2]

(c) Phenyl isocyanate and acetic anhydride give acetanilide.

In the oxygen ethers, the existence of an intermediate product due to the addition of the acid anhydride to the double bonding of the ether was assumed. With the thioethers the existence of such an addition-product was definitely proved.

Ethyl isodiphenyl thiourea and acetic anhydride can be heated to the boiling-point of the latter without seeming change, or the formation of ethyl acetate; and on careful treatment with alkali, the original base can be regenerated.

If, however, the excess of anhydride be decomposed with alcohol, the resulting oil is no longer soluble in dilute mineral acids. Alcoholic potash yields mercaptan and carbanilide, the decomposition taking place with great ease. An effort was made to purify this oil by dissolving in ether and washing with dilute sodium carbonate and water, and drying. The evaporation of the ether left a yellow oil insoluble in water and dilute alkalies. Experiment showed that alcoholic potash gave, on warming with this, mercaptan and diphenyl urea. Hence, if the body is the expected addition-product, it must decompose as follows :

$$\begin{array}{c} RNH \qquad SC_2H_5 \\ \diagdown C \diagup \\ RN \qquad OCOCH_3 \\ | \\ COCH_3 \end{array} + 2NaOH = (RNH)_2CO + C_2H_5SH +$$

$$2CH_3COONa + H_2O.$$
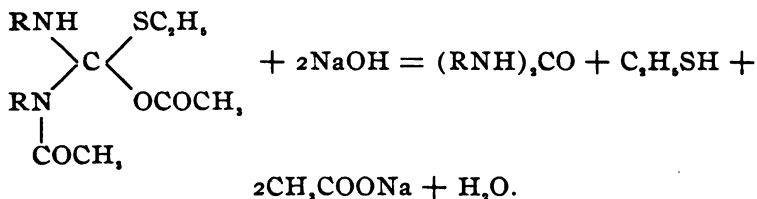
The oil was analyzed by dissolving it in alcohol, adding a definite quantity of standard sodium hydroxide, boiling with a reflux

[1] Gumpert (*J. prakt. Chem.*, 31, 121), who tried the action of phenyl isocyanate and acetic anhydride, obtained only acetanilide, a result probably due to moisture.

[2] Experiments have shown that diphenyl urea and boiling acetic anhydride give acetanilide and carbon dioxide.

condenser until decomposition was effected, and then titrating the excess of alkali, using phenol phthalein as an indicator. The amount of acetic anhydride could thus be determined, since 1 cc. normal alkali is equal to 0.05103 gram acetic anhydride.

    1. 1.7065 grams substance required 9.3 cc. alkali.

    2. 1.7965 grams substance required 9.76 cc. alkali.

	Calculated for $C_{19}H_{22}N_2O_2S$.	Found.	
		1.	2.
$(CH_3CO)_2O$ ···········	28.48	27.81	27.72

The difficulty of purifying such a compound, and the ease with which it breaks down, account for the low results. At high temperatures complete reaction follows between the acetic anhydride and the ethyl isothiocarbanilide. Thus, after heating at 190°, the tube opened with pressure due to inflammable gases, while mercaptan and ethyl acetate were recognized by the odor. The solid residue in the tube was pure acetanilide.

Action of Acetyl Chloride upon Ethyl Isothiodiphenyl Urea.— Experiments in a previous paper[1] have shown that with the oxygen urea ethers, acid chlorides react, giving, by addition and subsequent decomposition, ethyl chloride and acyl diphenyl urea. With the sulphur derivatives the reaction proceeds in an entirely different manner, due doubtless to the greater stability of the thio ethers toward acid reagents, and to the more negative character of the molecule. The general reaction between the thio-ethers and acid-chlorides is as follows :
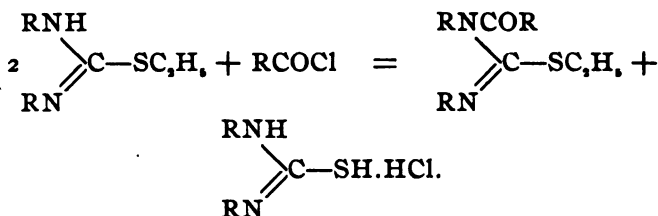
Either the anilido hydrogen is replaced directly by the acyl group, or there is first, addition to the double bond,
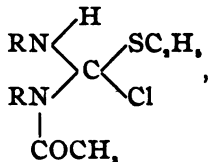
[1] This Journal, 21, 181.

and then loss of hydrogen chloride, which unites with a second molecule of the urea ether to form the hydrochloride.[1]

Two molecules of the thioether were dissolved in chloroform and treated with 1 molecule of acetyl chloride. After standing for twenty-four hours, the solution was washed with water, the excess of chloroform evaporated, and the residual oil taken up with ether; this was washed again with a solution of sodium bicarbonate to remove all traces of free acid. After drying, the evaporation of the solvent left a thick oil, which could not be crystallized, and was no longer soluble in dilute acid. This was analyzed, as in the previous case, by boiling in an alcoholic solution with a standard caustic alkali, the products being sodium acetate, mercaptan, and carbanilide.

1.3554 grams substance required 4.545 cc. normal NaOH. This is equivalent to 0.1954 gram CH_3CO.

	Calculated for $C_6H_5N{<}{COCH_3 \atop CSC_2H_5}$ C_6H_5N	Found.
CH_3CO	14.42	14.41

This body, monoacetylethylisodiphenyl thiourea, is interesting as being the first acyl derivative of the isourea ethers that has been isolated. The action of this substance toward glacial acetic acid has also a direct bearing upon the mechanism of the acetic anhydride reaction described on page 195.

Thus, when acetyl ethyl isodiphenyl thiourea was heated to the boiling-point with an excess of glacial acetic acid and allowed to stand for twenty-four hours, the product then being poured into water and purified as in the preceding cases, the original oil was recovered, and not an acetic acid addition-product identical with the product from acetic anhydride.

0.7420 gram oil required 4.9 cc. half-normal NaOH.

	Calculated for $C_{17}H_{18}ON_2S$.	Found.
CH_3CO....................	14.42	14.33

This points to the conclusion that the acetic anhydride acts by direct addition to the double bond, and not by first replacing the anilido hydrogen with an acetyl group and then adding acetic acid, as follows :

[1] *Am. Chem. J.*, 19, 136.

$$\begin{array}{c} \text{COCH}_3 \\ \diagup \\ \text{RNH} \qquad\qquad\qquad \text{RN} \\ \diagdown\text{C—SC}_2\text{H}_5 + (\text{CH}_3\text{CO})\text{C} = \diagdown\text{C—SC}_2\text{H}_5 + \text{HOCOCH}_3 \\ \text{NR} \qquad\qquad\qquad\qquad \text{RN} \end{array}$$

$$= \begin{array}{c} \text{COCH}_3 \\ \text{RN}\diagdown\diagup\text{SC}_2\text{H}_5 \\ \qquad\text{C} \\ \text{RN}\diagup\diagdown\text{OCOCH}_3 \\ | \\ \text{H} \end{array} .$$
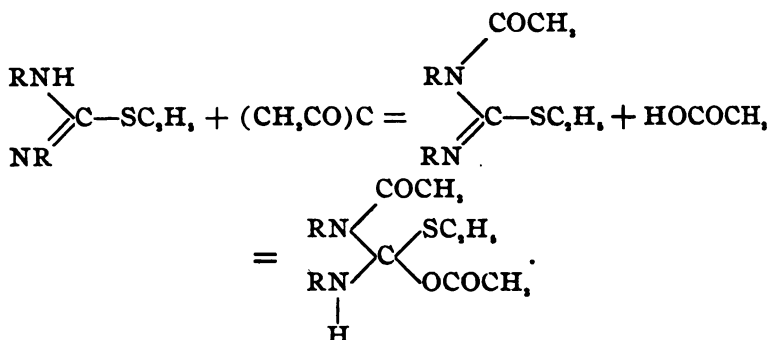
Action of Benzoyl Chloride.—Ten grams of ethyl isodiphenyl thiourea and 3 grams of benzoyl chloride were dissolved in benzene and allowed to stand for a week. The crystals that separated weighed 5.7 grams and consisted of the pure hydrochloride of the ethyl ether (m. p. 178°). After distilling off the benzene, an oil was left, insoluble in ammonia or dilute hydrochloric acid, the benzoyl ethyl thiodiphenyl urea. It was not obtained pure enough for analysis. An effort was made to distil the oil but decomposition ensued, with the formation of much tar, some phenyl isocyanate, and carbodiphenyl imide. Another portion heated in a sealed tube with hydrochloric acid, at 140°, gave ethyl chloride, carbon dioxide, mercaptan, aniline, and benzoic acid, so that while the body was not analyzed, its identity is fairly well established.

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March, 1900.

THE TECHNICAL ESTIMATION OF ZINC.

BY ALBERT H. LOW.

IN a report read June 11, 1892, before the Colorado Scientific Society, the method devised by the writer for the technical estimation of zinc in ores, etc., was approved as the best that had come to the attention of the committee. Although it had its weak points, some of which were recognized at the time, it was nevertheless well adapted for rapid and accurate work on the majority of Colorado ores and, in fact, no better method has since been offered.

Applications for a description of the method are very frequent, and in view of the fact that daily use in the laboratory for several years has naturally resulted in some changes from the original plan, it may not be out of place to again publish the scheme in its latest form. It is, of course, apparent that the method as given is not of universal application. Sometimes a fusion may be necessary to effect complete decomposition, or perhaps a preliminary treatment with hydrochloric acid may be required. (All hydrochloric acid must be expelled before beginning the regular treatment.) The operator is expected to recognize such cases and apply the remedy. He is cautioned, however, to be very careful about modifying the method except from actual necessity. Not that improvements are not possible, but it has been the writer's experience that most of the failures result either from inattention to details or the introduction of supposed improvements by the operator.

DESCRIPTION OF THE METHOD.

Standard Ferrocyanide Solution.—Dissolve 22 grams of potassium ferrocyanide crystals in water and dilute to 1 liter. Standardize as follows : Weigh carefully about 100 mg. of pure zinc and dissolve in 6 cc. of strong hydrochloric acid, using a 400 cc. beaker. Then add about 10 grams of ammonium chloride and 200 cc. of boiling water. Titrate with the ferrocyanide solution until a drop, when tested on a porcelain plate with a drop of a strong solution of uranium nitrate, shows a brown tinge. About 20 cc. of ferrocyanide will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing after each additional drop. Instead of using a single drop of the zinc solution for the test, the reaction is much sharper if several drops are placed in a depression of the plate and tested with a single drop of a strong uranium solution. As this is near the end of the titration the amount of zinc lost thereby is insignificant. As soon as a brown tinge is obtained, note the reading of the burette and then wait a minute or two and observe if one or more of the preceding tests do not also develop a tinge. The end-point is usually passed by a test or two and the burette reading must be accordingly corrected. A further correction must be made for

the amount of ferrocyanide required to produce a tinge under
the same conditions when no zinc is present. This is only 1 or
2 drops. One cc. of the standard solution will equal about 0.005
gram of zinc, or about 1 per cent. when 0.5 gram of ore is taken
for assay.

Assay of Ores.—To 0.5 gram of ore in a 250 cc. pear-shaped
flask, add about 2 grams of potassium nitrate and 5 cc. of strong
nitric acid. Heat until the acid is about half gone and then add
10 cc. of a cold saturated solution of potassium chlorate in strong
nitric acid and boil to complete dryness. It is usually necessary
to manipulate the flask in a holder over a naked flame to avoid
loss by bumping. The boiling may be conducted rapidly, and
towards the end it is best to heat the entire flask so as to expel
every trace of liquid. The potassium nitrate serves simply as a
diluent of the dry residue and insures the completeness of the
subsequent extraction of the zinc. Cool sufficiently and add 30
cc. of a prepared ammoniacal solution and heat to boiling. This
solution is made by dissolving 200 grams of ammonium chloride
in a mixture of 500 cc. of strong ammonia water and 350 cc. of
water. Boil the contents of the flask very gently for about two
minutes and then filter through a 9 cm. filter and wash with a
hot solution of ammonium chloride containing about 100 grams
of the salt and 50 cc. of strong ammonia water to the liter. Col-
lect the filtrate in a 400 cc. beaker. The insoluble residue should
be completely disintegrated and any ferric hydroxide present
should appear of a fine sandy nature. Place a bit of litmus
paper in the filtrate (not necessary if much copper is present),
and neutralize carefully with hydrochloric acid, finally adding 6
cc. of the strong acid in excess. Dilute to about 150 cc. and
add 50 cc. of a cold saturated solution of hydrogen sulphide.
Heat nearly to boiling and the solution is ready for titration. If
more convenient, or apparently advisable, pass a current of hydro-
gen sulphide gas through the hot solution diluted to 200 cc.
Copper and cadmium, which are interfering metals, are thus pre-
cipitated. Unless in large amount they need not be filtered off.
Practically no zinc is precipitated with the copper under these
conditions and the discoloration of the liquid by even 10 per cent.
of copper does not badly mask the uranium test. Titrate the

hot solution as follows : Pour off about one-third and set it aside in a beaker. Titrate the remainder, more or less rapidly, according as much or little zinc is indicated, until the end-point is passed, using the uranium indicator as in the standardization. Now add the greater part of the reserved portion and continue the titration with more caution until the end-point is again passed. Finally add the last of the reserved portion and finish the titration carefully, ordinarily two drops at a time. Make corrections of the final reading of the burette precisely as in the standardization. The true end-point is always slightly passed, and, after waiting a minute, it is usually sufficient to deduct for as many drops as show a brown tinge and one test additional.

Notes.—When precipitating with hydrogen sulphide it is a matter of considerable importance to have the solution qf a definite degree of acidity. Cadmium and copper are to be precipitated, while it is better to retain lead in solution and not unnecessarily blacken the liquid with its sulphide. If there is enough acid to prevent the precipitation of its sulphide the lead will not interfere in the titration. On the other hand too much acid will prevent the precipitation of the cadmium. It will not come down from a boiling hot solution containing 5 per cent. of strong hydrochloric acid. It is readily precipitated from a 3 per cent. solution while lead is not, if the liquid be nearly boiling. It is therefore recommended to have an excess of 6 cc. of strong hydrochloric acid in the final bulk of 200 cc. of solution.

Arsenic, when present in large amount, sometimes makes trouble by retaining iron in the ammoniacal solution. No attention need be paid to arsenic unless its presence in excess is thus indicated. In such a case begin anew and give the ore a preliminary treatment as follows :

To 0.5 gram of ore in the flask add 10 cc. of strong hydrochloric acid and 1 cc. of bromine. Warm very gently for several minutes to decompose the ore without loss of bromine and then boil rapidly to complete dryness. The arsenic will thus be sufficiently expelled. Now add the potassium nitrate and nitric acid and proceed in the usual manner.

In the case of ores that are free from cadmium, or where cadmium may be neglected, the copper may be readily precipitated without the use of hydrogen sulphide as follows : After neutral-

izing the ammoniacal filtrate from the insoluble residue, acidify
with an excess of 10 cc. of hydrochloric acid and add about 30
grams of granulated test lead.   Heat nearly to boiling and stir
the lead about until all the copper is precipitated.   Now dilute
to 200 cc. and titrate as described, without removing the lead
and precipitated copper.

DENVER, COLORADO, February 20, 1900.

A NEW BRIDGE ARRANGEMENT FOR THE DETERMINATION OF ELECTROMOTIVE FORCE BY AID OF THE LIPPMANN ELECTROMETER.

BY J. LIVINGSTON R. MORGAN.

THE two-bridge arrangements given by Ostwald[1] for the
measurement of electromotive force by the aid of the Lipp-
mann electrometer are the only two at present in use for pri-
mary cells. When an accumulator is used, it is only necessary to
connect it through a meter of manganine wire and to compensate
the cell to be measured by a fraction of the source taken off from
the wire by a sliding contact.[2] If a primary cell were used in
this way the results would not be accurate, owing to the decrease
in the electromotive force of the cell due to the small resistance
of the wire (50 ohms at most). Of the two methods in which
primary cells may be used as a source, we may say that each
is good for its purpose but that neither is of general utility.
The method using the sliding contact as already described for
an accumulator necessitates the use of a spool at one end
of the bridge wire, which contains thirteen times the resis-
tance of the bridge wire. In this way the cell is connected
through 700 ohms (14 × 50) so that its electromotive force remains
constant during the operation. By this, however, the drop in
potential at the ends of the wire, with a Leclanché cell (1.4 volts),
is only 0.1 volt, so that nothing larger than that can be measured,
unless some elaborate device is provided by which another
known electromotive force may be placed against the one to be

1 Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen, 252–253.
2 Ostwald : Grundriss der allgemeinen Chemie. 3d Ed., 43½ (1899).

measured so as to make the difference between the two less than 0.1 volt. The accuracy of the arrangement, however, is great, for each millimeter represents 0.0001 volt if the electrometer is sufficiently delicate.

In the other method the cell is closed through a resistance box of 1000 ohms provided with nine coils of 100 ohms and ten of 10 ohms each. If the Leclanché cell is cut down to one volt by a suitable resistance, then each of the 10-ohm coils represents 0.01 volt, while each of the 100-ohm coils represents 0.1 volt. By means of two plugs, any fraction of the 1 volt may thus be placed against the electromotive force to be measured until it is compensated. Thousandths of a volt may be approximated by the movement of the meniscus of the electrometer in opposite directions, caused by the connection first to a 10-ohm coil which is just too high, and then to one which is just too low. This, however, is not to be used with very delicate electrometers for 0.01 volt may cause the meniscus to go out of the field. By the box method, then, it is possible to measure any electromotive force, even above 1 volt if a battery of 1-volt cells is at hand, with an accuracy of 0.01 volt and to approximate to 0.001 volt.

We see then that the two methods separately give satisfactory results, but that it is inconvenient, to say the least, to measure anything above 0.1 volt, with an accuracy of more than about 0.002 volt. The object of this paper is to describe a method which can take the place of both those described, and measure directly, if the electrometer is delicate enough, any electromotive force with an accuracy of 0.001 volt, and can also be used at any time for rougher work just as conveniently as the box method.   . •

The current goes first through a box in which there are 13 coils of wire and then through a bridge wire of manganine (1 meter × 0.1 mm., resistance 50 ohms). Each of the 13 coils is of the same resistance as the wire on the bridge and may be made up of an equal length of the same wire properly insulated. On the wire there is a slider which is always in contact with the wire, while any number of the 13 coils can be brought into use in the same way as in the case of the box already mentioned. By this arrangement we have what is practically a bridge 14 meters

long of which the one meter laid out can be made any fourteenth
from 1 to 14. The wire from the plug on the coils and the
one from the sliding contact are treated just as those on the box
are (see figure). To make a determination, the slide on the
wire is placed at one end and the plug connected with the coils
is moved until one post gives too great an electromotive force
while the one next below it gives too small a one. The plug is
then left on this latter and the sliding contact on the bridge wire
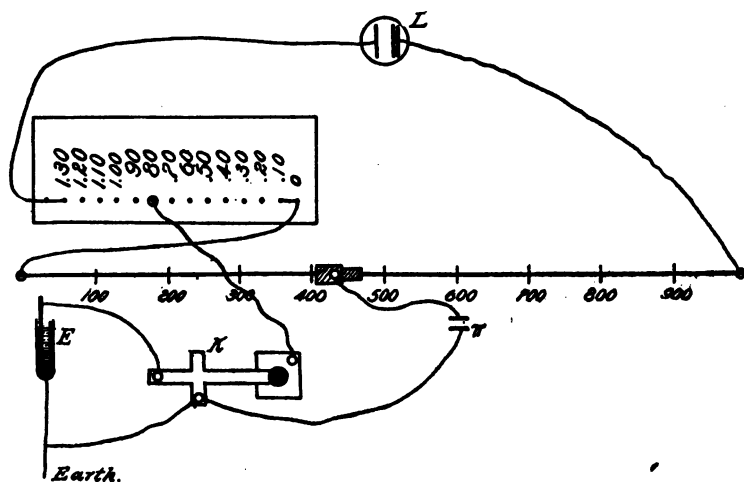
is moved until the meniscus in the electrometer is motionless when
the key is pressed. To the number opposite the coil, is then
added the same number of ten-thousandths as there are milli-
meters in the reading on the bridge. This number when mul-
tiplied by the total drop of potential at the connections to the
Leclanché gives the value in volts. Possibly the use of a storage
cell in the way described is to be preferred; although these
cells are uncertain as a rule in their results, still this method
just described has received a good trial and can be recom-
mended whenever a primary cell is to be used.

THE THERMOCHEMISTRY OF IRON AND STEEL.

[A WITHDRAWAL.]

BY E. D. CAMPBELL.

IN 1897 I published in connection with Mr. F. Thompson an article entitled " A Preliminary Thermochemical Study of Iron and Steel."[1] In this article some of the results given were so unusual, that it was deemed desirable to continue the work along the same lines of investigation. The work was taken up again in the autumn of 1897 by Mr. W. E. Hartman. The first experiments undertaken were to verify the results reported in our first paper as having been obtained by Mr. Thompson. Mr. Hartman was unable to duplicate the results obtained by Mr. Thompson and as a result of this I published " A Correction," in this Journal.[2]

During the past two years my three assistants, Messrs. W. E. Hartman, Carl Sundstrom, and E. C. Champion have worked independently in an effort to explain the very unusual results reported in our first paper. Our efforts have been towards eliminating the sources of error as much as possible ; to this end the calorimeter employed has been improved in many of its mechanical details, the time of solution has been reduced to usually less than four minutes. The rate of loss by radiation for each $0.1°$ has been determined as well as the slight gain in heat due to oxidation of cuprous chloride by dissolved air. With the most careful manipulation the difference between duplicate determinations could be kept down below 1 per cent. of the observed amount.

The first experiments undertaken were to determine the influence of the amount of free hydrochloric acid in the solution of ammonium cupric chloride employed. An interesting fact was developed at this point; it was found that if pure carbide of iron, $(CFe_3)_n$, isolated by electrolysis from annealed steel, was added to neutral ammonium copper chloride there was little or no action, the thermometer in the calorimeter rising less than $0.01°$ C. in five minutes; if, however, the ammonium copper chloride solution

[1] This Journal, 19, 754.
[2] Ibid., 20, 78.

contained 0.09 per cent. of free hydrochloric acid, there was marked action, and with 0.46 per cent. of free hydrochloric acid, solution of 1 gram of carbide was complete in two minutes.

Other experiments were made with increasing amounts of free hydrochloric acid up to 4 per cent., the amount used in our previous work, and although it was found that some free hydrochloric acid is necessary in order to obtain complete and rapid solution, the amount of free acid up to 4 per cent. did not appreciably influence the amount of heat evolved ; practically all of the iron was dissolved by its reaction with cupric chloride and not by direct solution in hydrochloric acid.   The solution finally adopted for all of the later work contained 0.84 per cent. of free hydrochloric acid.

The difficult solubility of carbide of iron in neutral ammonium cupric chloride will easily account for the results obtained by Osmond quoted in our first paper.   These results go to show that if steel be quenched or cold-rolled the heat of solution is thereby markedly increased.   The effect of heating and quenching steel as well as of cold-rolling is to render the carbide much more easily soluble in neutral solution than when existing in annealed metal.

The results of the experiments carried on during the past two years by Messrs. Hartman, Sundstrom, and Champion have agreed with each other within the limits of experimental error. These results all go to prove that the heat of solution of steel determined in slightly acid ammonium copper chloride is not varied at the outside more than 2 per cent. by variation in the heat or mechanical treatment of the sample nor by variations in chemical composition within the limits of ordinary steel.

In view of these later experiments it must be acknowledged that the results reported in our first paper have no foundations in fact, and I would therefore request that they be considered, if possible, as withdrawn.

I regret that results of experimentation which have not been confirmed by a second worker, should have been published from this laboratory.

ANN ARBOR, MICH., February 10, 1900.

[EDITORIAL NOTE : It would be unfair to print the above without reminding the reader that Dr. Campbell's eyesight was destroyed several years since in a laboratory accident, and in consequence he has since then been entirely dependent upon others in this respect].

FOREIGN COLORING-MATTER IN MILK.

BY ALBERT E. LEACH.

THE employment of artificial color by dishonest dealers to improve the appearance of milk has been practiced for many years, and while by no means as prevalent now as formerly, by reason of the stringent laws passed by various states regulating the sale of milk, the practice even to-day is by no means rare. Even in Massachusetts, which of all states is foremost in prosecuting the milk laws, artificially colored milks are occasionally found. Statistics of the Massachusetts State Board of Health show that out of 23,098 samples of milk collected throughout the state and analyzed during five years (from 1894 to 1898 inclusive), 151 samples or 0.6 per cent. were found to contain foreign coloring-matter. Of these samples, about 88 per cent. contained annatto, approximately 10 per cent. were found with an aniline orange, and about 2 per cent. with caramel.

Until comparatively recently, annatto was employed almost exclusively for this purpose. Caramel is least desirable of all the above colors from the point of view of the milk dealer, in that it is difficult to imitate with it the natural milk color by reason of the fact that the caramel color has too much of the brown and too little of the yellow in its composition. Annatto, on the other hand, when judiciously used and with the right dilution, gives a very rich, creamy appearance to the milk even when watered, which accounts for its popularity as a milk adulterant. Of late, however, the use of an orange aniline has been on the increase, and so far as a close imitation of the cream color is concerned, it is quite as efficient as annatto.

It is unfortunate for the milkman that artificial color of any kind is not analogous to the natural color of milk, which confines itself so largely to the cream. The artificial color, on the contrary, is dissipated through the whole body of the milk, so that when the cream has risen in a milk thus colored, the underlying layers, instead of showing the familiar bluish tint of skimmed milk, are still distinctly tinged below the layer of the fat, espe-

cially if any considerable quantity of the color has been used. This distinctive appearance is in itself often sufficient to direct the attention of the analyst to an artificially colored milk in the course of handling a large number of samples.

The addition of artificial color to milk is in most instances employed as a means of covering up evidences of watering, but this is not true in all cases. About 95 per cent. of the milks found colored in Massachusetts show, on analysis, the fraudulent addition of water. On the other hand, an orange aniline color was found by the writer in a milk containing over 17 per cent. of total solids, a conviction being secured on this case in court.

As to the nature of the orange aniline preparations employed for coloring milk, a few samples of these commercial "milk improvers" have fallen into the hands of the Department of Food and Drug Inspection of the Massachusetts Board of Health, and have proved, on examination, to be mixtures of two or more members of the diazo compounds of aniline. A mixture of what is known to the trade as "Orange G" and "Fast Yellow" gives a color which is practically identical with one of these preparations secured from a milk dealer and formerly used by him.

For purposes of prosecution or otherwise the generic name of "aniline orange" has been applied to this class of dyes in milk, and whatever particular mixture has been employed to make up the color, the tests which are given below have never failed to detect it when present in the milk.

The general scheme employed by the writer for the examination of milk samples suspected of being colored is as follows: About 150 cc. of the milk are curdled by the aid of heat and acetic acid, preferably in a porcelain casserole over a Bunsen flame. By the aid of a stirring rod, the curd can nearly always be gathered into one mass, which is much the easiest method of separation, the whey being simply poured off. If, however, the curd is too finely divided in the whey, the separation is effected by straining through a sieve or colander. All of the annatto or of the aniline orange present in the milk treated would be found in the curd, and part of the caramel. The curd, pressed free from adhering liquid, is picked apart, if necessary, and shaken with ether in a corked flask, in which it is allowed to soak for

several hours or until all the fat has been extracted and with it the annatto.   If the milk is uncolored, or has been colored with annatto, on pouring off the ether the curd should be left perfectly white.   If, on the other hand, aniline orange or caramel has been used, after pouring off the ether the curd will be colored more or less deeply depending on the amount of color employed. In other words, of the three colors annatto, caramel, and aniline orange, the annatto only is extracted by the ether.   If caramel has been used, the curd will have a brown color at this stage ; if aniline orange, the color of the curd will be a more or less bright orange.

The ether extract, containing the fat and the annatto, if present, is evaporated on the water-bath, the residue is made alkaline with sodium hydroxide and poured upon a small, *wet* filter, which will hold back the fat and, as the filtrate passes through, will allow the annatto, if present, to permeate the pores of the filter.   On washing off the fat gently under the water tap, all the annatto of the milk used for the test will be found to have been concentrated on the filter, giving it an orange color, tolerably permanent and varying in depth with the amount of annatto present.   The confirmatory test for annatto with stannous chloride may afterward be applied to the colored filter, producing the characteristic pink color.

The fat-free curd, if colored after the ether has been poured off, is examined further for caramel or aniline orange by placing a portion of the curd in a test-tube and shaking vigorously with concentrated hydrochloric acid.   If the color is caramel, the acid solution of the colored curd will gradually turn a deep blue on shaking, as would also the white fat-free curd of an uncolored milk, the blue coloration being formed in a very few minutes, if the fat has been *thoroughly* extracted from the curd ; indeed it seems to be absolutely essential for the prompt formation of the blue color in the acid solution that the curd be free from fat. Gentle heat will hasten the reaction.   It should be noted that it is only when the blue coloration of the acid occurs in connection with a *colored* curd that caramel is to be suspected, and if much caramel be present the coloration of the acid solution will be a brownish blue.   If the above treatment indicates caramel,

it would be well to confirm its presence by any of the usual tests on a fresh sample of the milk.[1]

If the milk has been colored with aniline orange, the colored curd, on applying the strong hydrochloric acid in the test-tube, will *immediately* turn pink. In the case of the caramel, the color of the curd itself remains unchanged, the solution only turning blue and that gradually ; on the contrary with the aniline orange the curd itself takes the pink color the moment the acid touches it. If a large amount of the aniline orange has been used in the milk, the curd will sometimes show the pink coloration when hydrochloric acid is applied directly to it, before treatment with ether, but the color reaction with the fat-free curd is very delicate and unmistakeable.

<div align="center">SUMMARY OF SCHEME FOR COLOR ANALYSIS.</div>

Curdle 150 cc. milk in casserole with heat and acetic acid. Gather curd in one mass. Pour off whey, or strain if curd is finely divided. Macerate curd with ether in corked flask. Pour off ether.

Ether Extract.

Evaporate off ether, treat residue with NaOH and pour on wetted filter. After the solution has passed through, wash off fat and dry filter, which if colored orange, indicates presence of annatto.
(Confirm by $SnCl_2$).

Extracted Curd.

(1) *If Colorless.* — Indicates presence of no foreign color other than in ether extract.

(2) *If Orange or Brownish.*—Indicates presence of aniline orange or caramel. Shake curd in test-tube with concentrated hydrochloric acid.

| If solution *gradually* turns blue ; indicative of caramel. (Confirm by testing for caramel in whey of original milk.) | If orange curd *immediately* turns pink ; indicative of aniline orange. |

THE REPEATED USE OF THE DOUBLE CHLORIDE OF COPPER AND POTASSIUM FOR THE SOLUTION OF STEEL OR IRON IN ESTIMATING CARBON.[2]

<div align="center">BY GEO. WM. SARGENT.</div>

IN the *Chemical News*, Vol. 79, p. 169, which appeared April 14 of last year, there is an article headed : " The Estimation of

[1] See Nineteenth Annual Report of the Mass. State Board of Health (1887), p. 183.

[2] Read at the March meeting of the Philadelphia Section of the American Chemical Society.

Carbon in Steel; Apparatus and Materials," signed J. T., in the course of which, it is stated, that the copper ammonium chloride may be reused as many as eight times, provided it is oxidized by drawing air through it after each solution, and provided the practice of allowing the sample to dissolve over night, is adopted. After the operation had been repeated four or five times, there was a decided decrease in the rate of solution and the speed of filtering, therefore it was practicable to use it successively but three or four times, unless the solution of the drillings was made in neutral copper ammonium chloride by shaking in a stoppered flask, when upon removing the carbon and oxidizing, the clear green liquid could be filtered from the iron oxide and reused *ad infinitem.*

Copper potassium chloride, owing to its freedom from organic matter, has supplanted the ammonium salt. Most chemists use the former in a hydrochloric acid solution,[1] when by the aid of a stirring machine, the drillings are dissolved in less than an hour. The reaction is expressed in the following equation:

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2.$$
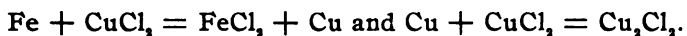
If now the cuprous chloride be oxidized to cupric, there is no reason why the double chloride solution should not be used repeatedly until the accumulated iron salts become too great. As stated above, this has been done, but the time consumed in oxidizing by a current of air was too long,—several days of an almost continuous current of air through a liter of the acid double chloride failed to completely oxidize the copper salt. The source of my air current was a filter pump, making the waste of water very considerable.

The oxidation was then attempted by the electric current using a cell such as is used for electrolytic oxidations. The result was fairly satisfactory, 3 quarts being oxidized in two days' time; but both these methods yield the cupric chloride at the expense of the hydrochloric acid:

$$O + 2HCl + Cu_2Cl_2 = H_2O + 2CuCl_2 \text{ and } 2HCl + Cu_2Cl_2 = H_2$$
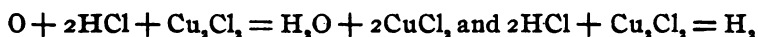
at the cathode and cupric chloride at the anode. Not knowing the quantity of acid consumed in the oxidation, without keeping careful account of the drillings and solution used, it would be

[1] See "The Chemical Analysis of Iron," by Blair.

difficult to tell just how much acid should be added after each oxidation in order to have the double chloride of the proper strength for the next solution. Again the chlorine formed at the anode would attack it. Therefore, I decided to try the effect of chlorinating the solution direct.

The result has been most agreeable. At the present time we have three bottles of 3 quarts' capacity; in the one, the filtered double chloride ready for the solution of the drillings is kept; the second receives the undiluted filtrate from the carbon, while the third, filled with the filtrates, stands in the corner of the hood with a current of chlorine gas passing through it. It requires just a day to chlorinate 3 quarts, and that is about the amount consumed each day. When chlorinated the solution, instead of being of a dirty brown, has almost the original color of copper potassium chloride. After standing over night in the hood and being filtered, the objectionable odor of chlorine is gone and the solution is again ready for use. The chlorinated double chloride is more energetic in its solvent action. In some instances the solution of the drillings has been accomplished in fifteen minutes.

As many as eleven solutions have been made with one quantity of the double chloride, and the time required for the eleventh solution and filtration was very little longer than for the first.

The following results were obtained by the successive use of the same solution:

Number of sample.	Carbon. Per cent.	Number of times the double chloride solution had been previously used.
17	0.864	None
"	0.864	1
1922	0.605	None
"	0.614	2
1930	0.755	None
"	0.752	3
1942	0.410	None
"	0.411	4
1944CX	1.608	None
"	1.614	6
1991	0.385	None
"	0.384	7
1969	0.613	None
"	0.615	11

The saving effected by reusing the copper potassium chloride solution is no inconsiderable amount, especially where much of the salt is used.   Roughly estimating, 1 pound of black oxide of manganese, and 1.5 pounds of hydrochloric acid, are sufficient to reconvert 3 quarts of the double chloride, worth about $1.00.

LABORATORY OF THE CARPENTER STEEL CO.,
    READING, PA., March, 1900.

ON THE DETERMINATION OF CARBON AND HYDROGEN BY COMBUSTION IN OXYGEN USING COPPER OXIDE.[1]

BY CHARLES F. MABERY AND WILLIAM R. CLYMER.
Received March 15, 1900.

IN a former paper[2] on combustion with copper oxide it was stated that some experiments were in progress to determine the conditions of efficiency, and limits of accuracy when applied to the analysis of oils containing only carbon and hydrogen.

In the long and tedious experience in the analysis of the great number of hydrocarbons that have been under examination in this laboratory, there have been ample opportunities to observe the working details in the hands of a large number of operators who have served at different times as assistants.

The difficulties in the way of securing results with oils containing only carbon and hydrogen, that will calculate closely to 100 per cent., are much greater than with substances containing smaller proportions of these elements, and require great skill and patience on the part of the operator.

Our experience shows that copper oxide is reliable after it has been brought to a constant condition by blank trials.   The gases that are evolved in the combustion of some of the hydrocarbons require the highest temperature in presence of oxygen that can be brought to bear, without too great strain on the combustion tube.

The first essential is a drying apparatus that will remove water and carbon dioxide from air and oxygen, and remain in good condition without too frequent renewal.   The apparatus now in

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[1] The work described in this paper formed the subject of a thesis by Mr. Clymer for the Degree of Bachelor of Science.

[2] This Journal, 20, 510.

use in this laboratory which does not need renewal oftener than once in a year or two, consists of two pieces of combustion tubing 1.75 meters long, with a bend 30 cm. from one end, with an angle of about 105°, and placed on the wall in front of the combustion furnaces. One of these tubes for air and another for oxygen are nearly filled with broken glass and concentrated sulphuric acid. A second set of tubes are filled to the same extent with glass and a 40 per cent. solution of potassium hydroxide, one for air and another for oxygen. Air is supplied from a large iron tank under water pressure and the flow is regulated by a mercury seal. Oxygen is supplied from a smaller tank under water pressure regulated by an overflow.

For absorbing water from combustion, there is no more convenient nor efficient means than concentrated sulphuric acid. One point must be borne in mind and that is the retention of carbon dioxide by the acid. Since it is well known that concentrated sulphuric acid dissolves carbon dioxide to the extent of 75 per cent. of its volume, some experiments were made to ascertain just the conditions necessary to avoid retention in analysis.

In one experiment dry carbon dioxide was passed for one hour through 2 cc. of the acid in a U-tube, just sealed by the acid. Then dry air was passed through the acid for two hours, when the tube was found to have gained 1 milligram in weight. At the end of another hour the gain was reduced to 0.0008 gram, and at the end of the third hour the weight was just the same as at the beginning of the experiment.

In a second experiment conducted in the same manner the original weight was reached in two and one-half hours. In a third experiment a larger sulphuric acid tube was used containing 7 cc. of the concentrated acid. After passing carbon dioxide for one-half hour and air for one hour and fifteen minutes the gain in weight was 0.0075. In continuing the passage of air at the rate of 500 cc. per hour for different lengths of time the following results were obtained.

Minutes.	Increase.
15	0.0058
15	0.0047
15	0.0037
1 hour	0.0029
1 "	0.0018
1 "	0.0018
1 "	0.0001

It was, therefore, only after air had been passed five hours that the weight was reduced to the original.   In a third experiment a potash bulb was placed in front of the sulphuric acid tube, and carbon dioxide was passed one hour, and air for one hour.   The potash bulb was now attached and the gain in weight (with air) compared with the loss in the acid tube.

Hour.	Loss in acid tube.	Gain in potash tube.
1	0.0014	0.0014
1	0.0008	0.0007
1	0.0005	0.0005
1	0.0002	0.0002
1	0.0000	0.0001

In a fourth experiment, carbon dioxide was passed for one hour through 2 cc. of acid, then air for one hour, then air for one hour more and weighed; the gain in weight was 0.0007 gram.   Carbon dioxide was then passed for one hour and air for another hour, then at the end of a second hour the weight was 0.0004 gram.   In three repetitions the gains were respectively 0.0006, 0.0004, and 0.0006 gram showing that passing air the same length of time leaves the same weight of carbon dioxide in the acid.   These experiments indicate that when a small volume of acid, 2 to 3 cc., is used with the large volume of oxygen and air used to expel carbon dioxide from the tube, very little of the gas remains dissolved in the acid.   But with larger volumes of the acid there is danger of retention of carbon dioxide.

In testing the capacity of sulphuric acid to retain moisture, moist air was passed through 2 to 3 cc. of the acid at the rate of 1100 cc. per hour for four hours.   At this rate the bubbles cannot be counted.   In front of the sulphuric acid tube was placed a high tube filled with phosphorus pentoxide but there was no gain in the latter tube.   There is therefore no danger of loss in water if sulphuric acid is used.   The only value of this experiment was to ascertain the conditions since Morley showed several years ago that sulphuric acid is a most efficient drying agent. The form of sulphuric acid tube we have used for several years has a bulb for collecting the greater part of the condensed water which is poured out after weighing.   The forward bend of the U is 10 cm. in height from the bottom and a side tube is attached for connection to the potash bulb.   When containing 3 cc. of concentrated acid, and 0.2000 gram water is weighed in each

combustion, the tube may be safely used without replacing the acid in ten or twelve combustions and probably longer. That sulphuric acid is preferable to calcium chloride has frequently been shown, since the best fused calcium chloride may contain basic chloride which retains carbon dioxide. It was shown by Winkler[1] that lime in the chloride cannot be completely saturated by carbon dioxide, since the inside of the granules remain caustic for a long time.

It is doubtful whether there is a more convenient apparatus than the Geissler potash bulb for the absorption of carbon dioxide, especially if the substance analyzed consists, for the most part, of carbon and hydrogen. There is no danger of loss of carbon dioxide if the solution of $33\frac{1}{3}$ per cent. potash be not used in more than four or five analyses. But there is danger of loss of moisture from the potash bulb unless care is taken to prevent it.

Some experiments were made to ascertain the conditions of safety. In one experiment the calcium chloride tube in front of the potash bulb was filled with freshly fused calcium chloride, broken to the size of grains of rice. Air was passed through at the rate of 550 cc. per hour with no loss in weight of the potash bulb, and the result was verified by placing a sulphuric acid tube in front of the calcium chloride tube which showed no gain in weight. Any faster rate than this showed a loss in the potash bulb and a corresponding gain in the sulphuric acid tube. On replacing the granular calcium chloride with other more finely ground, in a slightly longer tube, and passing air at the rate of 1050 cc. an hour, or 120 bubbles a minute, there was no change in weights. With a calcium tube of common length, 6 cm., a rate of 880 cc. per hour caused a loss of 0.0004 gram in the potash bulb and a gain of 0.0005 gram in the sulphuric acid tube. It is therefore safe to pass 500 cc. per minute through a tube filled with freshly fused finely granular calcium chloride. Such calcium chloride may be used in a considerable number of analyses. This rate can not be exceeded in the combustion of oils that are in part or all volatile without decomposition, or that yield gaseous products in burning. But this rate is in any sense in excess of the rate of evolution of gas from the combustion, since the carbon dioxide is, for the most part, immediately absorbed as

1 *Ztschr. anal. Chem.*, 545, 1882.

soon as it meets the potash solution. By replacing the fused calcium chloride with phosphorus pentoxide, there was no loss even when the rate exceeded 1000 cc. per hour, or 120 bubbles a second. But the oxide offers no advantages over the fused chloride in ordinary analysis.

In preparing for a long series of combustions a combustion tube should be selected that promises to stand 50 to 100 analyses, since it requires a long time to get the tube and its contents and connections in good working order. A long time is required to remove all the volatile impurities from the best copper oxide, and the moisture from the tube and oxide. Rubber stoppers are the only means for satisfactory connections, but before they become constant in weight probably some of the sulphur must be volatilized and moisture expelled. It is therefore necessary to test carefully all parts of the apparatus by means of blank experiments in the beginning, and even after the apparatus becomes constant it is well occasionally to apply a blank test.

In conducting analyses of such bodies as the high-boiling constituents of petroleum, the closest attention to details is necessary. The tube must be as hot as it will stand, and yet not hot enough to lessen its durability, on account of the labor involved in getting it in good condition. If the combustion tube be filled with oxygen before the substance is inserted and the rate of volatilization be carefully controlled, any hydrocarbon may be burned in a furnace with 20 burners. Many analyses were lost before these conditions were fully understood. In view of the possibility that a longer combustion tube might insure complete combustion and shorten the time of the analysis, two furnaces were placed together, and a tube nearly two meters in length was used. But the results were not more satisfactory than with a tube of ordinary length.

As a general summary of what is necessary to insure desirable accuracy in such determinations, it must be fully understood at the outset that no operation in analytical chemistry demands greater precautions, closer attention to details, or more skill and patience on the part of the operator to insure results within 0.20 per cent. of the maximum 100 per cent. in substances composed solely of carbon and hydrogen, such as petroleum oils.

In view of the great amount of work that will have to be done in determining the constitution of the large number of hydrocarbons with high molecular weights in Pennsylvania, California, and other petroleums, it would be a great advantage if a method for the determination of carbon and hydrogen could be devised that would avoid the tedious routine of the present method. But with present knowledge of this subject this method is probably all that can be hoped for. The Geissler potash bulb and the sulphuric acid tube seem to be as convenient forms as can be devised and they are capable, as shown above, of retaining carbon dioxide and water with as rapid delivery as is consistent with complete combustion. Rubber corks are objectionable, but they are the only convenient and reliable means of connection available.

We have tried successfully weighing the bulbs full of oxygen, thus avoiding the expulsion of oxygen by air. But since the time necessary to carry forward all the carbon dioxide is equivalent to that necessary to displace oxygen by air, there is nothing gained by weighing the bulbs filled with oxygen. The precautions necessary to insure cleanliness of the bulbs and constant conditions of moisture and temperature in weighing must be carefully observed.

CIDER VINEGAR : ITS SOLIDS AND ASH.

By R. E. DOOLITTLE AND W. H. HESS.

DURING the past few years the question of vinegar adulteration has received considerable attention from food chemists. Heretofore the sophistication has consisted almost entirely of the sale of colored distilled vinegar for pure fermented apple juice. As distilled vinegar contains little or no solids or ash this fraud was easily detected by very simple determinations. During the year 1899, however, there appeared for sale on the markets of this state, vinegar containing the necessary amount of solids and ash required by the statute for cider vinegar; but on ordinary analysis of this the solids and ash did not have the usual appearance of solids and ash of vinegar from pure apple juice. It was to ascertain the character of these vinegars

that the investigation of the solids and ash of cider vinegar was made.

THE SOLIDS.

The solids of pure cider vinegar consist of glycerol, albuminous substances, gums, malic and other organic acids, and mineral matter. The solids of pure cider vinegar give no rotation with the polariscope and little or no reducing action on Fehling solution after the customary clarification with lead acetate. Pure cider vinegar gives with lead acetate a heavy, flaky, light reddish brown-colored precipitate, which carries down with it all the coloring-matter leaving the solution above clear and nearly colorless. For analysis of solids 1000 cc. of pure cider vinegar was evaporated to a thick sirup on a water-bath and this residue taken up several times with distilled water and the water evaporated off to remove acetic acid. The suspected vinegars were treated in the same manner. The appearance of the solids on evaporation should be noted. Pure cider vinegar solids have a pleasant baked apple odor and are light and foamy in appearance. The spurious vinegars gave solids like molasses in appearance and of sharp acid odor. These residues gave the following results on analysis :

	Pure cider vinegar solids.	Apple pomace vinegar solids.	Suspected vinegar. (1)	Suspected vinegar. (2)	Boiled cider.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Reducing sugar before inversion.	0 to 14	0	42.88	56.82	61.12
" " after " .	0 to 10	0	33.36	57.04	66.45
Polarization before inversion.....	0	0	$+40.7°$	$-31.14°$	$-17.9°$
" after "	0	0	$+38.8°$	$-34.25°$	$-25.0°$

THE ASH, OR MINERAL MATTER.

The ash, or mineral matter, of pure cider vinegar consists principally of potash with small amounts of sulphuric anhydride, phosphoric acid, alumina, lime, magnesia, etc. The total amount should not be less than 0.25 per cent. For analysis, 100 cc. of the vinegar are taken for the determination of the total solids and ash in the usual way. The ash is dissolved in dilute hydrochloric acid and quantitative analysis made by the usual

method. The results in the following table are given as the average composition as determined by a large number of analyses. The suspected vinegars, Nos. "1" and "2," and also the ash of vinegar made by repressing moist fermented apple pomace, are given for comparison.

	Pure cider vinegar ash. Per cent.	Apple pomace vinegar ash. Per cent.	Vinegar. (1) Per cent.	Vinegar. (2) Per cent.
Calcium Oxide (CaO)	3.40 to 8.21	4.73	4.70	37.95
Magnesium oxide (MgO) ...	1.88 to 3.44	4.12	2.00	2.22
Potassium oxide (K₂O)	46.33 to 65.64	37.00	None	7.84
Sodium oxide (Na₂O).......	Trace to trace	Trace	49.71	Trace
Sulphuric anhydride (SO₃) .	4.66 to 16.29	34.78	27.04	12.74
Phosphoric anhydride (P₂O₅.	3.29 to 6.66	9.66	0.005	1.82
Iron oxide (Fe₂O₃)	None to trace	Trace	Trace	1.60
Carbon dioxide, loss, etc....	40.44 to 0	9.61	16.54	35.83

The results of these analyses plainly showed that suspected vinegar No. 1 was composed of dilute acetic acid, glucose, and soda-ash. Suspected vinegar No. 2 was a mixture of acetic acid, boiled cider, and lime.

LABORATORY MICHIGAN DAIRY AND FOOD DEPARTMENT,
March 12, 1900.

NOTES.

Test for Tin.—I have found the blue color produced by the action of stannous chloride upon ammonium molybdate to serve as a very delicate test for tin; and have had my students use it for the last few months with very good results. In working this process one should go through the usual separation, filter off the black flakes, dissolve them in hydrochloric acid, then take a few drops of this solution and add a little water and then some ammonium molybdate. Blue color shows the presence of tin.

To determine the delicacy of the test, I used a standard solution of stannous chloride, and noticed results obtained from the mercuric chloride and ammonium molybdate tests.

Strong solution of SnCl₂ gives a heavy blue precipitate; with mercuric chloride a heavy white precipitate.

A solution of SnCl₂ containing 0.000021 gram to 1 cc. gives a deep blue color; with mercuric chloride a faint cloudiness.

A solution of SnCl₂ containing 0.0000042 gram to 1 cc. gives a

faint blue color with ammonium molybdate; with mercuric chloride not even a trace of cloudiness.

I find that the ammonium molybdate as prepared in the laboratory gives the best results.

ALLEN ROGERS.

Professor C. F. Mabery has sent to the Paris Exposition, at the invitation of the United States Geological Survey, 150 specimens of products from petroleum, illustrating the composition of Pennsylvania, Ohio, Canadian, California, South American, and Japanese petroleums, and specimens of nitrogen compounds from California petroleum, and sulphur compounds from Canadian petroleum. Other specimens illustrate the composition of paraffin.

NEW BOOKS.

DESCRIPTIVE GENERAL CHEMISTRY. · BY S. E. TILLMAN, Professor of Chemistry, Mineralogy and Geology, United States Military Academy. Second Edition. New York : John Wiley and Sons. London : Chapman and Hall. x + 429 pp. 8vo. cloth. Price, $3.00.

This book was written to meet the requirements for a textbook on chemistry at the Military Academy at West Point. It aims to give in compact form the salient facts of chemistry that the professional soldier ought to know. The time available for the study of chemistry at the Academy is a little less than two-hundred hours, so that in order to cover the subject but a very limited amount of laboratory work can be undertaken. The chief aim therefore is to impart to the student the necessary information, rather than to make the element of mental discipline the more prominent one. Study of a text-book accompanied by recitations and experimental and explanatory lectures together with a small amount of selected laboratory work consequently make up the course pursued.

The book is divided into six chapters which are as follows: I. Essential Principles of Chemistry, pp. 1–58 ; II. Affinity, pp. 59–81 ; III. Non-metals, pp. 82–192 ; IV. Metals, pp. 193–310 ; V. Organic chemistry, pp. 311–356 ; VI. Applications of Chemistry, pp. 357–411. In the first chapter the general principles of chemistry are stated, while in Chapter II, the law of mass action, strength of acids and bases, theory of solution, electrolysis,

thermal chemistry, periodic law, etc., are discussed. All this is
of course done very briefly, and in connection with these two
chapters, in particular, the explanatory lectures mentioned above
will no doubt be very essential. Chapters III and IV are not
unlike chapters on the same subjects found in other texts. In
the 45 pages devoted to organic chemistry only a number of groups
of such compounds as are of the utmost practical importance to the
particular student for whom the text is intended could be con-
sidered. The applications of chemistry in the last chapter
include calorific value, explosives, fixed oils, dyeing, and the
manufacture of glass, pottery, coal-gas, beer, distilled liquors,
wine, bread, soap, leather, and cheese. While this chapter is
devoted to practical applications exclusively, the author has not
neglected to seize the opportunities of pointing out numerous
practical applications in the chapters preceding.

The author has earnestly endeavored to incorporate recent
discoveries and theories into his book. While his statements
are generally clear, they are unfortunately not always free from
inaccuracies. Only a few instances of this will here be men-
tioned. So on p. 69 the author neglects to point out that the
assumption of electrical charges on the ions is a salient part of
the theory of electrolytic dissociation, but simply adds in a foot-
note that the ions are probably electrically charged. On p. 71
heat of formation is confused with the thermal change that
accompanies a chemical reaction. On p. 99 the statement is
made that the form of the crystal is due to water of crystallization.

The book as a whole is good for the purpose for which it was
written. The selection of the topics treated (upon which so
much depends in a case like this) is wise ; and the presentation
is good considering the very condensed form necessitated. There
can be no doubt that the book will meet the special needs of the
students at the Military Academy better than any other text-
book that is available at present.

LOUIS KAHLENBERG.

LEITFADEN FÜR DEN UNTERRICHT IN DER ANORGANISCHEN CHEMIE. BY
DR. JOACHIM SPERBER. Zürich: Verlag von E. Speidel. 1899. 119 pp.

This is the first part of an extended treatise on inorganic
chemistry. It treats of the usual gaseous elements, the
halogens, and the non-metals. The author has applied the

inductive method to the teaching of inorganic chemistry. From simple and well chosen experiments, the fundamental principles are derived. Each set of experiments is chosen with the idea of illustrating some particular law, and is given in advance of the statement of the law itself. The laws of definite and multiple proportions, and Avogadro's law, are all established by experiment before the detailed study of the elements is begun. The order in which the separate elements are taken up is unusual. Beginning with hydrogen, the elements fluorine, chlorine, bromine, and iodine are studied, and then their hydrogen compounds. Subsequently oxygen, sulphur, selenium, and tellurium are taken up, and followed by their hydrogen compounds. Then comes the group of trivalent elements, nitrogen, phosphorus, arsenic, followed by the tetravalent carbon and silicon.

The statements in regard to the occurrence, preparation, properties, and uses of the separate elements are concise, accurate, and comprehensive. Separate theoretical considerations such as the dissociation of substances by heat, the determination of molecular weights, etc., are discussed in appropriate places, which tend to emphasize them and to show their applicability. The book contains the most recent discoveries. The illustrations are frequent, and exceptionally good. HENRY FAY.

LEXIKON DER KOHLENSTOFF VERBINDUNGEN. VON M. M. Richter. Zweite Auflage der " Tabellen der Kohlenstoff-Verbindungen nach deren empirischer Zuzammensetzung geordnet." Hamburg und Leipzig: Leopold Voss ; New York : G. E. Stechert. pp. about 3100. Price, 39 Lieferungen at M. 1.80 each.

It is, apparently, impossible to secure the adoption of a uniform system of nomenclature for carbon compounds. Indeed some chemists claim, and with good reason, that complete uniformity is not desirable. It becomes, therefore, every year more difficult to be sure of finding, in chemical literature, what is known about particular compounds. The work before us furnishes a lexicon of the carbon compounds arranged in accordance with their empirical formulas. The order is, first, that of the number of carbon atoms, second, that of the number of elements, third that of the elements other than carbon in the order :

$$H \ O \ N \ Cl \ Br \ I \ F \ S \ P \ Al \ldots \ldots Zr.$$

The only exception to a rigid use of the above classification

is in the case of salts, which are given under the corresponding
acids or bases.   After each empirical formula is given the per-
centage composition for all compounds containing only carbon,
hydrogen, oxygen, and nitrogen.   Then follows a list of all
known isomers of the given composition, giving melting-points
and boiling-points, references to the literature, and finally the
volume and page of the last edition of '' Beilstein '' where the
compound is described.   The number of compounds included in
the work is about 75,000, while the last edition of '' Beilstein ''
includes only 57,000.

The usefulness of the principle used for registering organic
compounds is so apparent that it has been adopted for the in-
dexes of the *Berichte* and of Liebig's *Annalen*.

The literature is fully covered to the end of 1898, and yearly
supplements are promised.

A few errors have been detected, but mostly where confusion
exists in the literature and a critical knowledge of the relations
involved was necessary to avoid mistake.   Even such errors are
probably rare and will seldom cause trouble in using the work.

The author complains that the failure to give empirical formu-
las, on the part of many writers, has added greatly to his labors
and requests that such formulas be always given.   In the opin-
ion of the writer it would be a misfortune if this request should
lead to the use of fewer structural formulas.   The needs and
advantage of the average reader are of greater importance than
the time of the lexicographer.   WILLIAM A. NOYES.

THE URINE AND THE CLINICAL CHEMISTRY OF THE GASTRIC CONTENTS,
    THE COMMON POISONS, AND MILK. BY J. W. HOLLAND, M.D., Professor
    of Medical Chemistry and Toxicology, Jefferson Medical College of
    Philadelphia.   Sixth edition, revised and enlarged.   Philadelphia:
    P. Blakiston's Son & Co.   49 illustrations.   Cloth.   Price, $1.00 net.

This syllabus for the laboratory aims to guide the student in
the chemical examinations that are of service to the physician.
The methods are much the same as may be found in similar
works, and, while in many instances they are well selected, they
include certain methods that might better be omitted or replaced
by procedures which yield results of clinical value.   The brief
text omits much information that would add materially to the
work.   It is particularly desirable to indicate more definitely to
what use the results obtained by the various methods are to be

put in practice, even at the risk of adding slightly to the bulk of the text. Unfortunately misstatements are not infrequent and there is an unusual number of errors in the references.

E. E. SMITH.

ANNUAIRE DU BUREAU DES LONGITUDES, pour l'An 1900. Paris : Gauthier-Villars. 18mo. 800 pp. Price, 1.85 francs.

This handy little annual is, as its name would indicate, mostly concerned with astronomic data. The first three hundred pages are devoted to calendars, astronomic phenomena of 1900, data of all kinds concerning the sun, moon, earth, planets, stars, and comets. Then follow tables of various weights and measures, moneys, statistics of population, territory and mortality in different countries. These are followed by diverse tables, such as magnetic intensity in various parts of France ; specific gravities of solids, liquids and gases; acoustic, optic, and electric data.

The scientific addenda contain a well-written article of thirty pages on "electric units," by A. Cornu ; an essay of over eighty pages on "dynamo-electric machines" also by Cornu, concise but satisfactorily written, and a short essay on "the new gases of the atmosphere," by Lippmann.

Many of the tables concerning physical and chemical facts are incomplete, and do not give the very best, latest determinations. In general, the French determination only is given, whenever a datum has been determined by a Frenchman, and his value stands until some other Frenchman does it better. This may be very patriotic, but it is not scientific, or good sense.

Visitors to Paris this year will be interested in the statement that "The legal time in France is that of the observatory of Paris, and is that recorded by the dials *outside* the stations, the dials *inside* the stations being several minutes later, for purely administrative reasons !" J. W. RICHARDS.

OPTICAL ACTIVITY AND CHEMICAL COMPOSITION. BY DR. H. LANDOLT, Professor of Chemistry in the University of Berlin. Translated with the author's permission by JOHN McCRAE, Ph.D. London : Whittaker and Co.; New York : The Macmillan Company. 158 pp. Price, $1.00.

This little book is a translation of the eighth chapter of the well-known Graham-Otto "Lehrbuch der Chemie," which has passed through several editions. This eighth chapter was contributed by Professor Landolt who is the great authority on

everything connected with the subject of the optical activity of organic compounds. The discussion in this book covers briefly the subject of optical activity in general and the relation of this activity to the composition and structure of various groups of organic compounds. It does not deal with the practical applications of polariscopic methods at all, this larger field being fully covered by the important work of the author, "Das optische Drehungsvermoegen organischer Substanzen, und dessen praktische Anwendungen," an English translation of which is now being made by the writer of this notice.

Dr. McCrae's translation is an extremely clear and creditable one and the book will undoubtedly be found useful.

J. H. LONG.

CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN. HERAUSGEGEBEN VON DR. GEORG LUNGE. Zweiter Band. 143 Abbildungen. Vierte Auflage. Berlin: Julius Springer, 1900. xii + 804 pp. Price, 16 marks.

This volume treats of Iron, by Th. Beckert; Other Metals, Metallic Salts, Dr. Pufahl; Fertilizers, Dr. O. Böttcher; Fodders, Dr. F. Barnstein; Explosives, O. Guttmann; Matches, Wladmir Jettel; Gas Manufacture, Ammonium Compounds, Dr. O. Pfeiffer; Coal Tar, Dr. H. Köhler; Inorganic Colors, Dr. Gnehm. In such a wide range of subjects some unevenness in treatment is inevitable. A careful examination of the book shows that in the main, the work has been well done though there are some omissions that will surprise the reader familiar with recent practice. For example, nothing is said of the methods for the determination of phosphorus in steel depending upon the reduction of molybdenum in the yellow precipitate and its determination by permanganate. Cupric ammonium chloride only is mentioned as a solvent for iron in carbon determinations. No reference is made either to the recent improvement in Jones' reductor or to Dr. Shimer's beautiful combustion method now so widely used. There are other omissions equally serious.

Rapid methods are absolutely essential in steel laboratories where the bulk of such work is done and any treatment which, like this, fails to give them proper prominence cannot be pronounced altogether satisfactory.

In a German book it is unusual to find so many references to American improvements. The Gooch crucible, Hoskins' gaso-

line furnace, Ricketts' rubbing plate, and Jones' reductor are all mentioned and some of them figured and there are numerous references to this Journal, to the *Journal of Analytical and Applied Chemistry*, and to the *Engineering and Mining Journal.* Drown's method for silicon is described as "Verfahren von Brown."

One feature of the book deserving of notice is the reprinting of the most useful tables on separate sheets. These are placed at the end of the book to be torn out and pasted up in the laboratory if desired. The mechanical execution of the book is excellent. The third volume is promised for the middle of 1900.

<div align="right">E. H.</div>

THE GRAMMAR OF SCIENCE. BY KARL PIERSON. Second edition revised and enlarged with 33 figures. London: Adam and Charles Black. 1900. New York: The Macmillan Co. 8 vo. xviii + 548 pp.

This is a metaphysical book written by a believer in scientific methods. It is divided into twelve chapters and an appendix. The chapters are entitled as follows: Introductory; The Facts of Science; The Scientific Law; Cause and Effect—Probability; Space and Time; The Geometry of Motion; Matter; The Laws of Motion; Life; Evolution (Variation and Selection); Evolution (Reproduction and Inheritance); The Classification of the Sciences; The mechanical execution of the book (printed by R. and R. Clark, Edinburgh) is superb. E. H.

ELEMENTARY CHEMISTRY FOR HIGH SCHOOLS AND ACADEMIES. BY ALBERT L. AREY. C. E. Rochester High School. New York: The Macmillan Company. 1899. xi + 271 pp. Price, 90 cents.

There seems to be an increasing tendency to introduce chemistry into the secondary schools as a disciplinary study. This volume is offered as a text-book in elementary chemistry, and is an attempt to present the subject in such a manner as to develop the student's faculties for observation and interpretation. This is accomplished by making the book a laboratory guide as well as a text-book. Numerous questions on the text and the laboratory experiments are found throughout the book. They have been intelligently selected, and are of such a nature that they can be answered only by direct experiment or by analogy. Many statements of facts have purposely been omitted so that the student may be more impressed with the experiment. The experiments are well selected and well arranged.

The main portion of the book treats of the elementary laws, the preparation, properties, and reactions of the gases, non-metals and metals. No mention of the periodic law is made, and there is no attempt to show the striking analogies in the properties of the elements and their compounds. It is much to be regretted also that there is little mention of historical names. They are so intimately connected with the science that it seems a great pity to have dropped them almost entirely. The author has introduced the term *crith* as the weight of a liter of hydrogen. It does not aid in the understanding and must surely lead to confusion.

The last chapter of twenty-five pages treats briefly of qualitative analysis. In the reviewer's opinion this portion of the book should have been devoted to the study of the preparation of typical inorganic compounds. The prime object of many books of this class is to prepare the student to make *separations*. While this cannot be said of this volume, there will, nevertheless, be a strong tendency on the part of the student to anticipate qualitative analysis on account of its presence in the book.

With the exception of the criticisms made, the book is to be commended.   HENRY FAY.

THE THEORY OF ELECTROLYTIC DISSOCIATION AND SOME OF ITS APPLICATIONS. BY HARRY C. JONES, Associate in Physical Chemistry in Johns Hopkins University. New York: The Macmillan Company. 1900. Cloth. xii + 289 pp. Price, $1.60.

This book contains a survey of the earlier physical chemistry, an account of the origin of the theory of electrolytic dissociation together with a presentation of the evidence supporting the same, and some of the important applications of the theory.

Every student of chemistry, physics, and biology, who is not already well acquainted with the theory of electrolytic dissociation will find this an interesting and valuable book to read. The development of modern physical chemistry is, in a large measure, intimately connected with this theory. The facts that the latter has been able to explain and to correlate are many; and above all, the importance of the stimulus it has given to research can hardly be overestimated.

In this book the theory of electrolytic dissociation is viewed in its most favorable light. It must be admitted, however, that during the last year or two, facts have begun to accumulate which

the theory cannot explain. Though these facts have developed mainly from a study of non-aqueous solutions, yet in many instances the theory finds much difficulty in explaining the facts in case of aqueous solutions, especially when quantitative data are involved. It seems at present that even before the theory of electrolytic dissociation will have found its way into regular chemical text-books, it will have undergone radical modifications from its present form, or will perhaps have been superseded by more adequate·explanations.   LOUIS KAHLENBERG.

VICTOR V. RICHTER'S ORGANIC CHEMISTRY OR CHEMISTRY OF THE CAR-
    BON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ. Authorized transla-
    tion by EDGAR F. SMITH, Professor of Chemistry, University of Penn-
    sylvania. Third American from the eighth German edition. Vol. II.
    Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son
    & Co. 1900. 671 pp. Price, $3.00.

The first volume of this work was reviewed last year.[1] About the only adverse criticism which could be made of the completed work is that the theoretical discussions are often so concise that it is almost impossible for beginners to comprehend them. It is, however, necessary, in a book of this character, to choose between a very concise style and the omission of a great deal of material which it is desirable to include. The book is, undoubtedly, much more valuable because the former alternative was chosen. The comprehensive character of the work. considering its size, is remarkable.

In discussing Ladenburg's prism formula for benzene on page 41 the author has, apparently, overlooked the fact that, since the reduction of ortho compounds gives derivatives of cyclohexane in which the substituents are combined with adjacent carbon atoms, the prism formula must be considered as positively disproved.

Professor Anschütz has availed himself of the aid of other workers who are specially conversant with particular fields and has so secured an accuracy of presentation which a single author could not hope to attain.   W. A. NOYES.

AN INTRODUCTION TO PHYSICAL CHEMISTRY. BY JAMES WALKER, Pro-
    fessor of Chemistry in University College, Dundee. New York:
    The Macmillan Company. 1899. 8vo. Cloth. x+335 pp. Price, $2.50.

A number of elementary treatises on physical chemistry have

[1] This Journal 21, 708.

recently appeared. Although Professor Walker's book is rather more voluminous than other works on the same subject intended for beginners, it does not pretend to give a complete or even systematic survey of physical chemistry. Its main object as expressed by the author is to be explanatory and to place the student in a position to profit by the study of the larger systematic works of Ostwald, Nernst, and van't Hoff.

The book is divided into 27 chapters; and, though the enumeration is somewhat long, there is perhaps no better way to convey an idea of the .contents of this treatise than to indicate the subjects of these chapters together with the number of pages devoted to each. The chapters are as follows:—Units and Standards of Measurement, pp. 1–7; The Atomic Theory and Atomic Weights, pp. 8–21; Chemical Equations, pp. 22–26; The Simple Gas Laws, pp. 27–29; Specific Heats, pp. 30–37; The Periodic Law, pp. 38–49; Solubility, pp. 50–59; Fusion and Solidification, pp. 60–72; Vaporization and Condensation, pp. 73–83; The Kinetic Theory and Van der Waals' Equation, pp. 84–96; The Phase Rule, pp. 97–116; Thermochemical Change, pp. 117–126; Variation of Physical Properties in Homologous Series, pp. 127–135; Relation of Physical Properties to Composition and Constitution, pp. 136–147; The Properties of Dissolved Substances, pp. 148–157; Osmotic Pressure and the Gas Laws for Dilute Solutions, pp. 158–168; Deductions from the Gas Laws for Dilute Solutions, pp. 169–175; Methods of Molecular Weight Determinations, pp. 176–192; Molecular Complexity, pp. 193–200; Electrolytes and Electrolysis, pp. 201–216; Electrolytic Dissociation, pp. 217–233; Balanced Actions, pp. 234–253; Rate of Chemical Transformation, pp. 254–265; Relative Strengths of Acids and Bases, pp. 266–282; Equilibrium between Electrolytes, pp. 283–295; Applications of the Dissociation Theory, pp. 296–310; Thermodynamical Proofs, pp. 311–332.

The general treatment is non-mathematical, a few thermodynamical proofs in the last chapter being the only exceptions. The book really includes nearly all the important topics usually taught in classes in physical chemistry. The absence of a chapter on photochemistry may be noted, as may also the treatment of Nernst's theory of the E. M. F. of galvanic cells. The

order in which the subjects are considered is different from the usual one. Without going into details concerning this point, it may suffice to say that the manner in which the separate chapters are written is such as to weave them together in a logical way. The author seeks to have the student connect physical chemistry with his previous chemical knowledge so as to make the new subject of real use to him.

Clearness of statement characterizes the book throughout. The relative amount of space devoted to some of the subjects is perhaps open to some criticism; so, for example, the subject of thermal chemistry is treated in ten pages. The author, however, does not intend this to suffice but directs the student to the treatise of Muir and Wilson on this subject.

In the discussion of the applications of the dissociation theory the author has wisely chosen to content himself almost entirely with a merely qualitative treatment, since the quantitative side of this subject (especially whenever it involves the combination of the law of mass action and the theory of electrolytic dissociation) leaves much to be desired.

The book is indeed an introduction to the study of physical chemistry, for a perusal of its pages will give the student a knowledge of general, fundamental facts and will lead him to further inquiry. The author is clearly not one of those who believe that the subject of physical chemistry is already in a high state of perfection and that there is but little left to do except to fill in the details. It is to be regretted that the book does not contain more references to original articles.

LOUIS KAHLENBERG.

WATER AND WATER SUPPLIES. BY DR. JOHN C. THRESH. Second revised edition. vii+438. pp. Philadelphia: P. Blakiston's Son & Co. 1900.

Although this is called the second, revised edition of this work, it is an exact reproduction of the 1896 English edition, the only revision apparent being the correction of typographical and other errors in the first edition. It is nevertheless, a convenient handbook on water supplies.

The first part of the book treats of water, its composition, properties, etc.; the various sources of water supplies, as rain, surface, subsoil, spring, deep-well, and river water; the amount

and character of the water derived from these various sources; the nature and source of the impurities that may gain access to these different waters; and analyses of water supplies derived from these various sources. Then follow several chapters on the quality of drinking-waters; the effects upon health of impure waters; the interpretation of water analyses; the pollution of drinking-water; the self-purification of rivers. The purification of water, both on the large scale and for domestic purposes is treated of in subsequent chapters.

There is also a chapter on the laws relating to water supplies as comprised in the different special acts of Parliament with reference to the powers of individuals, towns and water companies, and likewise the various restrictions which have been raised in order to maintain the purity of natural water supplies.

The information contained in the book is drawn from the large personal experience of the author and from the voluminous literature on the subject. In this respect the author has shown considerable appreciation of the experiences of American investigators, especially the pioneer work performed in the study of filtration of water and sewage by the Massachusetts State Board of Health.

In discussing the interpretation of water analyses the author states that "Although a mere analysis cannot guarantee us purity and safety, yet it very frequently can reveal to us impurity and risk. When the source of a water, upon most careful examination by an expert, is found to be free from all danger of pollution, and the chemical examination proves that the inorganic constituents are unobjectionable, both in quantity and quality, and that organic matter is absent or present in barely appreciable amount, then safety, so far as human foresight can be trusted, may be guaranteed . . . . Chemical analysis, therefore, has its use; it is only when it is made the sole arbiter between safety and risk that it is abused, and is liable to lead to errors fraught with most disastrous consequences. Let the analysis be as careful and complete as possible, but let the results always be interpreted in the light afforded by a searching examination of the source of the sample."

At the close of the chapter he says: " Bacteriological, microscopical, and chemical examinations must always be associated

with a thorough investigation of the source of the water, to ascertain the possibility of contamination, continuous or inter- mittent. Then, and then only, if everything be satisfactory, we may be justified in speaking of safety and of freedom from risk; but where either bacteriological, microscopical, or chemical examination is unsatisfactory, the inquiry into the history of the water must be most careful and complete, and a guardedly-ex- pressed opinion given only after a full consideration of the bear- ing of the one upon the other.''

It is gratifying to read such positive statements with regard to the analysis of water for sanitary purposes because it is too fre- quently the case that either the chemist, bacteriologist, or the microscopist, or each of these, places undue value upon his results. Quite frequently all three forms of examination are necessary to form a definite idea as to the relative purity of a water. The author's long experience as an analyst and medical officer of health renders his opinion in this respect all the more valuable. D. H. BERGEY.

A TREATISE ON CRYSTALLOGRAPHY. BY W. J. LEWIS, M.A., Professor of Mineralogy in the University of Cambridge. Cambridge University Press. 8mo. 604 pp. Price, 14 shillings, net.

This is one of the most pretentious treatises on this subject which has appeared in the English language. The important, and, from a crystallographic standpoint, historic chair which the writer holds, has naturally given to his work a decidedly conserv- ative tone, from which many modern students will differ.

There are ten chapters (140 pages) dealing with the general geometric properties of crystals; seven chapters (300 pages) on the different systems; one chapter (100 pages) on twin crystals; and two short chapters on '' divers notations'' and goniometers, respectively.

The chapter on the formation of crystals is fragmentary and altogether too brief. The same is to be said of the chapter on "the law of constancy of angle." '' Symmetry'' is introduced clumsily but illustrated satisfactorily. The chapter on '' axial representation'' is somewhat labored; many of the points could have been just as satisfactorily proved by less cumbersome geo- metrical proof. The heavy Euclidean methods are tedious. The chapter on zone-indices and relations of zones is well stated, and,

didactically, is perhaps the best chapter in the book ; the chapter on the " anharmonic ratio" is also well done. Two chapters on crystal drawings and projections are satisfactory except for some more roundabout proofs, and the omission of all reference to gnomonic projection—an omission much to be deplored, for a projection which shows all zones as straight lines, instead of great circles, is surely worthy of 'the crystallographer's best attention.

The chapter on " The Systems" is unphilosophically written and, from a non-English point of view, indefensible. No attempt is made to explain clearly the philosophy of the matter. No clear proof is given why only 32 classes of forms (Groth's) are possible, and no satisfactory explanation of the peculiarities of the systems is attempted. The fact that Dr. V. Goldschmidt[1] has *proved* the unscientific nature of Groth's classification, and that the optical, thermal, electric as well as geometric properties of crystals all point to the six commonly accepted systems as the bases, the units, the fundamentals of crystal classification,— all this is overlooked. The old notion of making rhombohedral crystals into a seventh system is revived, although none of the physical properties of such crystals differentiate them from the hexagonal system ; and further yet, Miller's axes of reference are retained instead of substituting the Bravais, which are universally conceded as better and more logical. This is one of the worst examples of unwise conservatism in the book.

The seven chapters on the systems are thoroughly and conscientiously worked out. Particularly praiseworthy are the large number of actual specimens described as examples, most of these being descriptions of crystals in the Cambridge Museum. The concrete examples thus furnished are a great help to understanding the text, besides being valuable crystallographic data in themselves.

The long chapter on twinning is lucidly written, and enriched by drawings and data concerning many interesting specimens from the Cambridge collections. It is the best chapter in the book.

Taken altogether, it is a good exposition of old-school crystallography, with the addition of Groth's classification, rather unskilfully presented. The details of crystal forms, calculations,

[1] *Ztschr. Krys.*, January, 1899.

twins, etc., are well done, and the book is chiefly valuable to the advanced student for this information. For beginners, or as an introduction to the main principles of crystallography, it is unsuited, for it is not sufficiently didactic in tone nor clear in presentation, while making the primary error of misconceiving the fundamentals of crystal classification.

The paper, type and drawings are first class, the binding rather frail, and the uncut edges an abomination.

<div align="right">JOSEPH W. RICHARDS.</div>

BEGINSELEN DER SCHEIKUNDE. Door M. C. SCHUYTEN. Antwerpen. 1889. pp. 110. 8 vo.

The author of this little volume, who is professor at the Institute for Higher Studies in Brussels, as well as at the Technical School of Antwerp, has prepared for elementary classes a book on the rudiments of inorganic chemistry including chemical analysis. Naturally, in so small a compass some topics have to be treated superficially ; thus spectrum analysis is dealt with in one page and three lines; half a page is given to the properties useful in determining minerals, and this is followed by a table giving the names, composition and chief properties of 84 minerals.

In the preface the author explains that he has adopted the sound principle to "go from the known to the unknown." The book is excellently printed, a variety of types assisting comprehension. The few illustrations are sectional. Questions are introduced to aid teacher and pupil.

<div align="right">H. C. B.</div>

THE KINETIC THEORY OF GASES. Elementary Treatise with Mathematical Appendices. BY OSKAR EMIL MEYER. Translated from the second revised edition by ROBERT E. BAYNES. London, New York, and Bombay : Longmans, Green, & Co. 1899. xvi + 472 pp. 8vo. Cloth. Price, 15 shillings.

The first German edition of this treatise appeared in 1877, the first half of the second edition in 1895, and the second half in 1899. We have in the book before us the translation of the complete second edition.

In this revised edition the general plan of the first edition has been followed. The book is divided into three parts, together with six mathematical appendices. The subjects treated are as

follows: Part I. Molecular Motion and Its Energy, pp. 3–145; Part II. The Molecular Free Paths and the Phenomena Conditioned by Them, pp. 149–296; Part III. On the Direct Properties of the Molecules, pp. 299–352. The mathematical discussions connected with the treatment of these subjects are contained in the Appendices, pp. 355–466; they make no claim to completeness. While the contents of the book are limited to the same general range of phenomena considered in the first edition, an explanation on the kinetic theory of the resistance of air and of the reaction of a jet, together with an investigation concerning the influence of the dissociation of the molecules of a vapor upon its viscosity, have been inserted.

The author deserves much credit for the manner in which he has worked up the bulky literature of the subject which has accumulated during the past two decades. The translator has provided the English speaking public with a good translation of this valuable work. He has not added anything new except a few foot-notes, but he has provided an index that is an exceedingly valuable addition to the book.

Of late, criticisms of the kinetic theory of gases have frequently been heard, and it has even been charged that the theory has outgrown its usefulness and that it has done more harm than good. Nevertheless these very critics still gladly reach out for the kinetic theory whenever it can be used to explain some of their own pet theories, particularly those relating to the analogy between gases and solutions.

English-speaking scientists, and chemists in particular, will welcome this new English edition of Professor Meyer's excellent book.

The work of the publishers is very commendable.

<div style="text-align:right">LOUIS KAHLENBERG.</div>

LABORATORY MANUAL. EXPERIMENTS TO ILLUSTRATE THE ELEMENTARY PRINCIPLES OF CHEMISTRY. BY H. W. HILLYER, PH.D., Assistant Professor of Organic Chemistry in the University of Wisconsin. 200 pp. New York : The Macmillan Co. 1899. Price $1.90.

The "book is written for the use of college students of general chemistry." The first and much the larger portion of the book, (Part I.) is devoted to the preparation and properties of the elements and their compounds; another portion (Part II;) presents a limited number of quantitative experiments for the

verification of quantitative laws : the appendix contains needful data for the students' use. In the selection of experiments the author provides for beginners, for those possessing slight familiarity with the subject, and for those who have had a satisfactory laboratory course in the preparatory school. The experiments are well chosen and graded, the directions are carefully stated, and the questions are plainly those of a painstaking teacher. The directions to the student regarding his preliminary preparation for each laboratory exercise are, in particular, excellent. The book is well printed and excellently bound.

<div align="right">H. P. TALBOT.</div>

VOLUMETRIC ANALYSIS, SPECIALLY ADAPTED TO THE REQUIREMENTS OF STUDENTS ENTERING FOR THE ADVANCED PRACTICAL CHEMISTRY EXAMINATIONS OF THE SCIENCE AND ART DEPARTMENT. By JOHN B. COPPOCK. London : Whittaker & Co.; New York : Macmillan & Co. 12mo. pp. 92. Price, 50 cents.

The nature of this book is sufficiently indicated in the title. There is nothing contained in it worthy of special mention. It is chiefly notable for its omissions. Such books are of little value except to those who wish to pass an examination and have no further interest in the subject.   E. H.

BOOKS RECEIVED.

Leitfaden für den Unterricht in der anorganischen Chemie. Didaktisch bearbeitet von Dr. Joachim Sperber. Erster Teil. Zürick : Verlag von E. Speidel. 1899. 120 pp. Preis, M 2.40.

A Description of Some Chinese Vegetable Food Materials and their Nutritive and Economic Value. By Walter C. Blasdale. Bulletin No. 68, U. S. Department of Agriculture, Washington, D. C. 1899. 48 pp.

Preservatives in Canned Foods. Bulletin No. 165. 8 pp. Butter Adulteration. Bulletin No. 166. 12 pp. The North Carolina College of Agricultural and Mechanical Arts, Raleigh, N. C. 1899.

A Treatise on Crystallography. By W. J. Lewis, M.A. Cambridge : At the University Press. 1899. xii+612 pp. Price, 14 shillings net.

The Urine ; and Clinical Chemistry of the Gastric Contents, the Common Poisons, and Milk. By J. W. Holland, M.D. Sixth Edition, Revised and Enlarged. Philadelphia : P. Blakiston's Son & Co. 1899. vii +124 pp. Price, $1.00.

Index to the Literature of Zirconium. By A. C. Langmuir and Charles Baskerville. City of Washington : Published by the Smithsonian Institution. 1899. 8vo. 29 pp.

The Chemistry of Essential Oils and Artificial Perfumes. By Ernest J. Parry. London : Scott, Greenwood & Co. ; New York : D. Van Nostrand Co. 1899. viii+411 pp. Price, $5.00.

A System of Instruction in Qualitative Chemical Analysis. By Arthur H. Elliott and George A. Ferguson. Third Edition. 1899. Published by the Authors. 115-119 W. 68th St., N. Y. City. 155 pp. Price, $1.50.

Traité de la Fabrication des Liqueurs et de la Distillation des Alcools. Par P. Duplais, ainé. Septième édition, entièrement refendue par Marcel Arpin et Ernest Portier. Tome Premier—Les Alcools. 613 pp. 8 fr. Tome Second. Les Liqueurs. 606 pp. 10 fr. 1900. Paris : Gauthier-Villars. Quai des Grands-Augustins, 55.

The Cost of Living as Modified by Sanitary Science. By Ellen H. Richards. New York : John Wiley & Sons. 1899. 121 pp.

Beginselen der Scheikunde. Door Dr. M. C. Schuyter. Antwerpen : Jos. Ishoven, Van Straelenstraat, 8. 1899. 109 pp. Price, $1.50.

Agricultural Experiment Station of the University of Minnesota. Bulletin No. 63.—Miscellaneous Analyses, Composition of Tomatoes, Proteids of Wheat Flour. 50 pp. Bulletin No. 65.—Soil Investigation. 84 pp. 1899. St. Anthony Park, Minn.

The North Carolina Agricultural Experiment Station, Twenty-second Annual Report ; Bulletin No. 152-163. Contents.—Reports of officials; poultry notes ; vinegar adulteration ; the adulteration of coffee and tea; baking powders; the adulteration of flour ; mineraline ; the fertilizer control for 1898; horticultural experiments during 1896; digestive experiments; drinking water; farming in North Carolina ; rational stock feeding; the flora of North Carolina; preservatives in canned foods; butter ; poultry experiments; field and forage experiments; feeding experiments and milk records. lii+462 pp. Raleigh, N. C.

Lexikon der Kohlenstoff-Verbindungen. Von M. M. Richter. Zweite Auflage der "Tabellen der Kohlenstoff-Verbindungen nach deren empirischer Zusammensetzung geordnet." Thirty parts. 2000 pp. Price, M. 1.80, per part.

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Water and Water Supplies. By John C. Thresh. Second revised edition. Philadelphia : P. Blakiston's Son & Co. 1900. xv+438 pp. Price, $2.00.

Baking Powders. A treatise on the character, methods for the determination of the values, etc., with special reference to recent improvements in phosphate powders. By Charles A. Catlin. Published by the Rumford Chemical Works, Providence, R. I. 1899. 44 pp.

Water and Water Supplies. By John C. Thresh. Second revised edition. Philadelphia : P. Blakiston's Son & Co. 1900. xv+438 pp. Price, $2.00.

Annuaire pour l'An 1900, publié par le Bureau des Longitudes. Avec des Notices scientifiques. 628 pp. Les Machines Génératrics de Courants Électriques. Par M. A. Cornu. 89 pp. Les nouveaux Gaz de l'Atmosphere. Par M. G. Lippmann. 15 pp. Les Travaux au Mont Blanc en 1899. Par M. J. Janssen. Sur l'Application de l'Aéronautique. Par M. J. Janssen. 2 pp. Discours prononcés a l'Inauguration de la Statue de Félix Tisseraud. 19 pp. Liste des Membres qui Composent le Bureau des Longitudes. 37 pp. Paris : Gauthier-Villars, quai des Grands Augustins, 55. In one volume. Price, 1 fr. 50 c.

The Kinetic Theory of Gases. Elementary treatise with mathematical appendices. By Dr. Oskar Emil Meyer. Translated from the second revised edition by Robert E. Baynes. New York : Longmans, Green & Co. 1899. xvi + 472 pp. $4.00.

Elementary Chemistry for High Schools and Academies. By Albert L. Arey, C. E. New York : The Macmillan Co. 1899. xi + 271 pp. Price, 90 cents.

Introduction to Physical Chemistry. By James S. Walker, D.Sc., Ph.D. London & New York : The Macmillan Co. 1899. x + 335 pp. Price, $2.50.

Fifth Annual Report of the Montana Agricultural Experiment Station (Bulletin No. 20). 34 pp. Sheep Feeding (Bulletin No. 2). 13 pp. Agricultural Experiment Station, Bozeman, Montana.

Optical Activity and Chemical Composition. By Dr. H. Landolt, Professor of Chemistry in the University of Berlin. Translated with the Author's permission by John McCrae, Ph.D. New York : The Macmillan Co. 1899. xi + 158 pp.

Dietary Studies of Negroes in Eastern Virginia in 1897 and 1898. By H. B. Frissell and Isabel Bevier. Bulletin No. 71, U. S. Department of Agriculture, Washington, D. C.

The Theory of Electrolytic Dissociation and Some of its Applications. By Harry C. Jones, Associate in Physical Chemistry in Johns Hopkins University. New York : The Macmillan Company. 1900. xii + 289 pp. Price, $1.60.

The Slate Belt of Eastern New York and Western Vermont. By T. Nelson Dale. Extract from the Nineteenth Annual Report of the Survey, 1897-98. Part III.—Economic Geology. Washington : Government Printing Office. 1899. 155 pp.

Sheep Feeding. By J. H. Stewart and Horace Atwood. Bulletin No. 61. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 12 pp.

A Study of the Effect of Incandescent Gas-light on Plant Growth. By L. C. Corbett. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 24 pp., with numerous plates.

Commercial Feeding Stuffs in the Connecticut Market. Connecticut

Agricultural Experiment Station, New Haven, Conn. Bulletin No. 130, January, 1900. 40 pp.

Twenty-third Annual Report of the Connecticut Agricultural Experiment Station for 1899. Part I.—Fertilizers. New Haven, Conn. 92 pp.

Victor von Richter's Organic Chemistry or Chemistry of the Carbon Compounds. Edited by Prof. R. Anschütz (assisted by Dr. G. Schroeter). Authorized translation by Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Third American, from the Eighth German Edition. Volume II.—Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co. 1900. xvi + 671 pp. Price, $3.00.

The Elms and Their Diseases.—Bulletin No. 84. 25 pp. with plates. Commercial Fertilizers.—Bulletin No. 85. 53 pp. Kentucky Agricultural Experiment Station, Lexington, Ky.

Annuaire de l'Observatoire Muncipal de Paris, dit Observatoire de Montsouris, pour l'Année 1900. (Analyse et Travaux de 1898.) Meteorologie—Chemie—Micrographie. Applications a l'Hygiene. Paris: Gauthier-Villars. xii + 578 pp. Price, 2 fr.

A Pocket-book for Chemists, Chemical Manufacturers, Metallurgists, Dyers, Distillers, Brewers, Sugar Refiners, Photographers, Students, etc. By Thomas Bayley. Seventh Edition, revised and enlarged. London: E. & F. N. Spon; New York: Spon & Chamberlain. 1900. 559 pp. Price, $2.00.

Volumetric Analysis. Specially adapted to the requirements of students entering for the advanced practical chemistry examinations of the science and art department; also the intermediate science and preliminary scientific examinations of the University of London. By John B. Coppock, F.C.S., Inter. B.Sc. (Lond.). London: Whittaker & Co.; New York: The Macmillan Co. 1899. 92 pp. Price, 50 cents.

Analyses of Commercial Fertilizers and Paris Green. Bulletin of the Agricultural Experiment Station of the Louisiana State University and A. & M. College, Second Series, No. 58. 90 pp.

The Work of the Agricultural Experiment Stations on Tobacco. Abstracted by J. I. Schulte, with introduction and comments by Milton Whitney. U. S. Department of Agriculture, Report No. 63. Washington, D. C. 1900. 48 pp.

ERRATUM.

In the number for February, 1900, p. 139 line 10, for

" $[(CH_3)_2NH]_2TeCl_6$ " read " $[(CH_3)_2NH] TeCl_6$. "

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

NOTES ON SELENIUM AND TELLURIUM.

BY EDWARD KELLER.

IN a paper under the above title,[1] published some years ago, I pointed out the difference of behavior of selenium and tellurium, in the dioxide state, towards sulphur dioxide and ferrous sulphate in solutions of hydrochloric acid of various strength. The experiments were conducted under definite conditions, as stated in my original paper, the quantities of the two elements being in every case 0.1 gram each, the quantity of the solution 100 cc., and the acidity varying from 0.5 to 100 per cent., the pure hydrochloric acid meaning the aqueous product of 1.175 sp. gr. Based on quantitative determinations of the two elements precipitated by sulphur dioxide in the cold, and other conditions as already stated, the conclusions reached, were as follows: Selenium is most readily precipitated by sulphur dioxide in stroug hydrochloric acid. This precipitation continues to be complete until an acidity of 25 per cent. is reached, the solution being allowed to stand about twenty hours. The precipitation, within that time, becomes nil at an acidity of approximately 3 per cent. The precipitation of tellurium in strong hydrochloric

1 This Journal, 19, 771.

acid is nil. It begins with an acidity of about 80 per cent. (the time of standing as above), becomes complete at about 60 per cent., and continues to be so until the acidity is reduced to about 10 per cent.

On page 774 of the paper cited is found the following remark : " From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over 80 per cent. acid a separation is possible" (meaning a separation of selenium and tellurium).

A NEW METHOD OF QUANTITATIVE SEPARATION OF SELENIUM AND TELLURIUM.

That selenium is more readily precipitated by sulphur dioxide than tellurium has long been known and the principle has been practically applied, but, it seems, never to quantitative analysis. Since the publication of my paper, above referred to, I have had occasion in numerous instances to determine the two elements in copper analysis, and I have in all cases applied this hydrochloric acid-sulphur dioxide method. When working with a Gooch filter and a suction pump (filter-paper, of course, cannot be used) this separation is a rapid and simple one. My mode of operation is as follows : 100 grams of copper with from 2 to 4 grams of ferrous sulphate, are dissolved in 400 cc. nitric acid (sp. gr. 1.42) and the nitrous fumes expelled. This solution, after diluting and cooling, is made sufficiently ammoniacal to dissolve all the copper. After boiling and settling, the ferric hydroxide containing the selenium and tellurium is gathered on a filter. It must be freed from copper by washing with ammoniacal water, redissolving in acid, and reprecipitation with ammonia (repeatedly if necessary). This ferric hydroxide is then brought into dilute hydrochloric acid solution (not more acid being used than is necessary to dissolve the precipitate), and hydrogen sulphide passed through the cold liquid until saturation. The solution must be cold to retain the selenium sulphide in soluble form in sodium sulphide, and copper must be absent to guard against insoluble cupric selenide. The sulphides are filtered and washed and digested with a solution of sodium sulphide, which latter takes up the sulphides of selenium and tellurium. The solution, after filtering, is acidified with

nitric acid and evaporated to dryness. The latter operation must
be performed with care, to avoid loss of selenium dioxide. The
residue now contains the dioxides of selenium and tellurium and
sodium nitrate, besides some sulphur. To this residue is added
200 cc. of strong hydrochloric acid, and boiled until all the nitro-
hydrochloric acid (its presence being due to the nitrate) is de-
stroyed, and the two elements, which may have been oxidized to
the selenic and telluric form, are reduced to the selenous and
tellurous state. After cooling, the solution is filtered off from
the sulphur and the insoluble halide through a Gooch filter, and
the residue washed several times with strong hydrochloric acid;
the latter, however, need not be of more than 90 per cent.
strength. The filtrate is now ready to be saturated with sul-
phur dioxide gas, conveniently generated by copper borings and
concentrated sulphuric acid, which will precipitate the selenium
alone under the given conditions. After settling, which may be
accelerated by warming, the selenium is gathered on a weighed
Gooch filter and washed with hydrochloric acid (90 per cent.)
about three times. Here the filtrate is set aside, and the sele-
nium freed of salts, etc., by washing successively with warm, di-
lute hydrochloric acid, pure water, and strong alcohol. After
drying it is weighed. The filtrate containing the tellurium is
increased to double its volume with pure water. With the small
quantities of tellurium present in copper, the amount of sulphur
dioxide held in solutioᵢ is generally sufficient to precipitate that
element completely upon boiling ; however, it is safer to boil
the dilute solution for some minutes, and while doing so to con-
duct more sulphur dioxide through it. After cooling and settling,
the tellurium is filtered, washed, and weighed in the same man-
ner as the selenium.

   The following quantitative determinations, for which commer-
cial accuracy only is claimed, were made in proof of the method,
the conditions being that 0.1 gram of selenium and 0.1 gram of
tellurium, previously converted into dioxide, were jointly dis-
solved in 100 cc. of 90 per cent. hydrochloric acid, and the fur-
ther operations performed as previously described :

DETERMINATION OF SELENIUM AND TELLURIUM BY PRECIPITATION WITH SULPHUR DIOXIDE IN HYDROCHLORIC ACID.

Selenium.		Tellurium.	
Weighed in. Gram.	Found. Gram.	Weighed in. Gram.	Found. Gram.
0.1000	0.0983	0.1000	0.0998
0.1000	0.1000	0.1000	0.0986
0.1000	0.1006	0.1000	0.1010
0.1000	0.0994	0.1000	....
0.1000	0.1002	0.1000	0.0993
0.1000	0.1010	0.1000	0.1013
Av'r'ge 0.1000	0.0999	0.1000	0.1000

The selenium in every case proved to be free of tellurium by its complete solubility in potassium cyanide. Nor could selenium be detected in the filtrates with ferrous sulphate by either increasing or decreasing the strength of the acid. In short, the separation is complete.

In a paper by Mr. Victor Lenher[1] are to be found the following remarks : " When sulphur dioxide is brought into contact with such a strong solution, selenium should be precipitated free from tellurium according to Keller. When sulphur dioxide was introduced into this solution a red precipitate formed, showing selenium just precipitated. It appeared to darken, however, when the liquid was saturated. On boiling, the precipitate agglomerated into a mass which much resembled selenium, but on separating it by means of potassium cyanide it was found to consist of 3.2 grams of selenium and 28.3 grams of tellurium. This seems to indicate that tellurium and selenium cannot be perfectly separated by sulphur dioxide in strong hydrochloric acid solution."

Mr. Lenher worked with 5 pounds of tellurous and selenous material. He does not mention the quantity of acid he used. His conditions were, therefore, probably radically different from those as given in my own experiments.

As I could not doubt my own results of often repeated tests, nor Mr. Lenher's assertions, I inferred that the difference in the conclusions arrived at must be due to the difference in the relative masses of tellurium and acid present in the experiments, and I corroborated this by a few simple tests : The oxides of 0.1 gram of selenium and 5 grams of tellurium were dissolved in

[1] " Preparation of Metallic Tellurium," This Journal, 21, 347.

100 cc. of 90 per cent. hydrochloric acid, and the solution saturated with sulphur dioxide. The precipitate, after standing about twenty hours, contained all of the selenium with 2.1 grams of tellurium. In the subsequent tests the acid of the same strength was increased each time by 50 cc., the quantities of selenium and tellurium remaining constant. The quantity of tellurium decreased in each successive precipitation, and became nil when the quantity of acid reached 450 cc. It follows, therefore, that to obtain a perfect separation of selenium and tellurium in strong hydrochloric acid solution by means of sulphur dioxide, the quantity of acid must be about 100 times that of the tellurium.

Numerous chemists have pointed out the error made in determining tellurium in its metallic state, it being due to slight oxidation. Mr. F. H. D. Crane[1] found this error to be from 0.3–0.6 per cent. over the correct result, when no precautions were taken. Criticism for using this method in industrial practice seems to me entirely unjustified. Although accuracy is always essential, the practical chemist must be able to discriminate between accuracy and pedantry. For example: Our copper rarely contains as much as 0.01 per cent. of tellurium, and we should find, according to Mr. Crane, when using 100 grams of copper, from 0.01003 to 0.01006 instead of 0.01 gram of the element, a difference absolutely beyond detection and of no importance whatsoever in ordinary work. In fact, the chemist would find, in practice, that with more scientific methods ± 3 or 6 per cent. would often be far from covering the differences between his own duplicates, or those of other equally conscientious workers. In substantiation of this I need only refer to the determination of small percentages of precious metals,[2] upon which large commercial interests depend. With silver, which occurs in larger quantity than tellurium, determinations often differ ± 3 to 5 per cent. from the mean. With gold, occurring in smaller quantities, these variations rise as high as ± 25 per cent.

BALTIMORE, March, 1900.

[1] "A Contribution to the Knowledge of Tellurium," Dissertation, Johns Hopkins University, 1898.

[2] "Assays of Copper and Copper Matte," Trans. A. I. M. E., 25, 250.

THE ESTIMATION OF ALUMINA AND FERRIC OXIDE IN NATURAL PHOSPHATES.[1]

BY F. P. VEITCH.

THE search for an accurate and rapid method for the determination of alumina and iron oxide in the presence of phosphoric acid has occupied the attention of analysts for years, and many methods have been proposed for this difficult operation. It may be said generally that even those methods that have stood the tests of extended use have not escaped severe criticism ; they are only accurate within narrow and rigidly defined limits or they are tedious and time-consuming.

Aside from its interest from the scientific point of view, this subject is of importance in its technical and commercial aspects. The value of raw mineral phosphates, which, in the United States alone, for the year 1893, Wiley estimates at $4,157,070,[2] is determined largely by their content of alumina and iron.

In phosphatic slags the estimation of these oxides is more difficult, though possibly not so important.

SOURCES OF ERROR IN THE OLDER METHODS.

The Glaser alcohol, the acetate with its various modifications, and the caustic alkali, methods as carried out by Lasne, Lichtschlag, and by Gladding, have all been severely criticized and the following sources of error pointed out by various observers:[3]

1. In the Glaser alcohol method, the precipitation of manganese with the iron and aluminum phosphates, and solubility of the phosphates in the wash-water. Probably the manganese can be eliminated by a second precipitation in the presence of a large amount of ammonium chloride. Possibly the presence of a large amount of ammonium sulphate may also effect the accuracy of this method, in those cases where the excess of ammonia is com-

pletely removed by boiling. Aluminum phosphate is noticeably soluble in a strong sulphate solution, which is neutral or faintly acid from SO_3.

2. In the acetate method and its variations, the precipitation of the lime with the iron and aluminum phosphates, solubility of aluminum phosphate in cold acetate solutions, solubility and dissociation of iron and aluminum phosphates in water,[1] also when the phosphates are fused with sodium carbonate, and the iron determined by precipitation with ammonia, the contamination of the iron with calcium phosphate, which is not always entirely decomposed by fusion. Of these the most serious sources of error are the first and the last mentioned.

3. In the caustic alkali methods, there is danger of some of the aluminum being held by the voluminous precipitate produced by the alkali; there is also danger of alumina being precipitated if much carbon dioxide is absorbed; Lasne and Lichtschlag have shown that while the method is long it gives accurate results if properly conducted. Blaltner and Brasseur[2] have recently investigated the more important methods and conclude:

"The acetate method should be discontinued; figures for alumina are nearly always too low."

Glaser method (alcohol) gives accurate results in the absence of manganese.

The caustic soda method, as carried out by Lasne, gives exact results. Gruber's and Gladding's methods are condemned.

In view of these many sources of error in the conventional methods, considerable time has been devoted to the study of a method that, it is hoped, is free from most of the above-mentioned objections. It is an adaptation, so far as possible, of the good points of the present best methods. From the precipitating reagent, it may be designated

THE THIOSULPHATE METHOD.

The use of a soluble thiosulphate for the separation of alumina from iron and aluminum from several other metals seems to be due to G. Chancel.[3] Later it was used by Stead and by Car-

[1] *Chem. Zlg.* (1897), p. 264; also Fresenius.
[2] *Bull. Soc. Chim.* [3], 17, 18, No. 15.
[3] *Compt. rend.*, 46, 98.

not;[1] by the latter for the separation of aluminum as phos-
phate, in the presence of ammonium acetate, from iron. Lasne[2]
also uses it to precipitate aluminum phosphate in the presence
of ammonium acetate, after removing iron, lime, etc., with caus-
tic soda.

From the available literature on the subject it seems that a
method based on the separation of aluminum phosphate from
iron and lime by a thiosulphate and ammonium chloride alone,
may be used for the determination of aluminum in the common
natural phosphates.

Considerable work has been done with the method to gain
familiarity with it and to test its applicability under various con-
ditions and in the presence of various salts. For this work a
chemically pure aluminum sulphate was prepared in which
alumina has been carefully determined. This salt was used for
all the tests.

The preliminary work under varying conditions, following the
method as laid down by Chancel and by Carnot, did not always
give concordant results, frequently being low. A brief study
suggested the cause of this, and the addition of a considerable
quantity of ammonium chloride led to much better results. The
principle upon which the method is based is the insolubility of
aluminum phosphate in a strong neutral solution of ammonium
chloride. The thiosulphate has nothing to do with the precipi-
tation, except that it is an exact method of obtaining the desired
neutrality. Thomson[3] has devised a method in which he makes
use of this principle, neutralizing with ammonia, using a delicate
indicator to determine neutrality.

Study of the Proposed Method.—One of the first problems pre-
sented in the study of any method for the determination of
alumina as phosphate is the composition of the ignited phosphate.
Observers do not agree as to this. While all agree that the nor-
mal phosphate is only obtained in the presence of an excess of
phosphoric acid, they do not agree that it is always obtained,
even under these conditions.[4]

1 Blair's " Chemical Analysis of Iron," second edition, 185, 186.

2 *Bull. Soc. Chim.*, 15, 118.

3 *J. Soc. Chem. Ind.*, 15, 868.

4 *Chem. Ztg.* (1897), pp. 264, and 21, 116; Wiley's " Principles and Practice of Agri-
cultural Analysis," Vol. II, p. 24 ; Blair's " Chemical Analysis of Iron," second edition,
185; S. C. Agr. Expt. Sta., Bull. No. 2.

Wash Solutions.—It seems that the solution of this problem can only be obtained by a study of the solutions used in washing the precipitate. Besides waters of all temperatures, solutions of various salts, such as 5 per cent. ammonium nitrate, ammonium chloride, 1 per cent. ammonium nitrate plus 0.02 per cent. ammonium phosphate, and dilute ammonium acetate, have been proposed and used by many investigators. These various washes possibly account for the variations from the normal, so frequently noted. In the brief mention of some of the observed sources of error in the conventional methods it was shown, by numerous authorities, that the recently precipitated phosphates of iron and aluminum, when freed from adhering salts, are slightly soluble, or rather are dissociated, in water of any temperature. Those who have apparently used water successfully as a wash probably did not wash enough, only three or four times, to remove the adhering salts. Cold ammonium or sodium acetate also slowly dissolves aluminum phosphate.

The effects of the following wash liquors have been studied :

Water at from 60° to 70° C.

5 per cent. ammonium nitrate at from 60° to 70° C.

1 "   "   "   "   "   "   60° " 70° C.

5 "   "   "   "   and 0.02 per cent. ammonium phosphate at from 60° to 70° C.

Method of Study.—Various quantities of the C. P. aluminum sulphate were placed in a 12-ounce beaker with a solution of 2 grams of ammonium phosphate, the resulting precipitate dissolved in hydrochloric acid, and 25 cc. of a 50 per cent. solution of ammonium chloride added. The solution was then made alkaline with ammonia and the precipitate just dissolved with hydrochloric acid, noting approximately the number of cubic centimeters required after the solution had become acid ; the solution was then diluted to about 250 cc., and for each cubic centimeter of hydrochloric acid added to the acid solution 5 cc. of a 50 per cent. solution of ammonium thiosulphate were added dropwise, the beaker covered with a watch-glass, the solution boiled half an hour, filtered, washed, dried, and ignited to constant weight.

The results are given in Table I. All results in the work have been corrected by blank determinations on the reagents

F. P. VEITCH,

TABLE I.

Wash solution.	Washings. Times.	Washings. Volume. cc.	Al₂O₃. Theory. Mgs.	Al₂O₃. Found. Mgs.	Error. Mgs.
Water 60° to 70° C..............	40	500	159.7	155.9	—3.8
" 60° " 70° C..............	20	250	39.9	38.2	—1.7
5 per cent. ammonium nitrate, 60° to 70° C........	20	250	39.9	39.8	—0.1
5 " " " 60° to 70° C........	20	250	79.8	79.6	—0.2
5 " " " 60° to 70° C........	20	250	79.8	80.1	—0.3
5 " " " 60° to 70° C........	50	650	79.8	78.9	—0.9
5 " " " 60° to 70° C........	50	650	79.8	79.3	—0.5
1 " " " 60° to 70° C........	20	250	39.9	39.3	—0.6
1 " " " 60° to 70° C........	20	250	79.8	79.2	—0.6
1 " " " 60° to 70° C........	20	250	79.8	78.8	—1.0
1 " " " 60° to 70° C........	20	250	79.8	77.4	—2.1
1 " " " 60° to 70° C........	20	250	79.8	79.2	—0.6
1 " " " 60° to 70° C........	20	250	79.8	79.2	—0.6
5 (NH₄)₂NO₃+0.02 per cent. (NH₄)₂HPO₄	20	250	79.8	80.9	—1.1
5 " " "	20	250	79.8	80.2	—0.4

employed ; and all precipitations were made in the presence of an excess of phosphoric acid.

An examination of the table shows that, of the wash solutions, 5 per cent. ammonium nitrate washing twenty times gives practically theoretical results. As many as 50 washings with this solution give results slightly low but still good. The other solutions were rejected as they showed a decided solvent effect, except the ammonium nitrates plus ammonium phosphate, upon prolonged washing. Twenty washings were required to free the precipitate from chlorides, sulfates, and ammonium phosphate. In all succeeding work 5 per cent. ammonium nitrate was used, washing twenty times unless otherwise stated. Long heating with the blast, ten to twenty minutes, was required to reduce to constant weight.

Composition of the Ignited Aluminum Phosphate.—The phosphoric acid, in the aluminum phosphate washed twenty times with 5 per cent. ammonium nitrate, was carefully determined by precipitation with molybdate solution, washing the precipitate of ammonium phosphomolybdate with dilute nitric acid, and washing the final precipitate free of chlorides.

	Theory. P_2O_5. Mgs.	Found. P_2O_5. Mgs.
a	58.2	58.8
b	...	58.7
c	...	58.8
		Average, 58.8

The salt obtained under the above-mentioned conditions seems to be the normal phosphate, $AlPO_4$.

THE EFFECT OF THE PRESENCE OF SALTS OF SOME OTHER METALS.

Effect of Iron Salts.—Five grams of ammonium ferric alum dissolved in water, 2 grams of ammonium phosphate added, and treated as for aluminum phosphate, washing twenty times with ammonium nitrate, gave :

	Calculated as alumina. Mgs.
a	4.5
b	0.0
c	1.3
d	0.0

Precipitated while slightly warm.

Another series precipitated twice gave:

	Calculated as alumina. Mg.
a	0.4
b	0.0
c	0.0
d	0.0

Solutions containing aluminum sulphate, ammonium phosphate, and 5 grams of ammonium ferric alum precipitated once with ammonium thiosulphate, gave:

	Theory. Mgs.	Al$_2$O$_3$ found. Mgs.
a	78.9	86.4
b	23.9	28.2

Both contained iron.

Similar solutions precipitated twice with sodium thiosulphate, gave:

	Theory. Mgs.	Al$_2$O$_3$ found. Mgs.
a	39.9	39.4
b	39.9	40.8

These precipitates contained no iron.

Therefore, in the presence of large quantities of ferric iron, two precipitations only are necessary to separate the iron.

Effect of Calcium Salts.—Two grams of calcium phosphate, precipitated once, gave:

a, Nothing.

b,   "

Aluminum phosphate plus 2 grams calcium phosphate, precipitated once, gave:

	Theory. Mgs.	Al$_2$O$_3$ found. Mgs.
a	79.8	80.1
b	79.8	80.8
c	79.8	81.0
d	23.9	24.3
e	79.8	·80.2
f	79.8	79.3

a, *b*, *c*, and *d* were washed twenty times with 5 per cent. ammonium nitrate; *e* and *f* were washed fifty times.

The error produced by the presence of calcium salts alone is

not so great as that produced by iron salts. In ,this case it seems probable that the error is produced by the well-known property of the aluminum precipitates of carrying down other salts mechanically. Two precipitations separate completely aluminum phosphate from very large quantities of iron and of lime, as is shown by the following data :

$Al_2(SO_4)_3$. Gram.	$Ca_3(PO_4)_2$. Gram.	$NH_4Fe(SO_4)_2$. Gram.	Al_2O_3 Theory. Mgs.	Al_2O_3 Recovered. Mgs.
½	½	¼	39.9	39.6
¼	½	¼	19.9	18.8
¼	½	¼	19.9	18.8
½	2	1 iron	39.9	39.7
½	2	1 "	39.9	39.9

From the foregoing results the conclusion seems warranted that aluminum phosphate can be quantitatively separated by a soluble thiosulphate and ammonium chloride from a hydrochloric acid solution of iron, alumina, and lime phosphates containing only a small amount of sulphates. The statement of many observers, that theoretical results on aluminum phosphates can only be obtained in the presence of an excess of phosphoric acid, has been confirmed by my own work. The error produced by precipitating a second time without adding phosphoric acid amounted in some cases to 2 mgs. alumina.

The Effect of Magnesium, Sodium, and Potassium Salts.—Three solutions containing in 50 cc. the following :

	A. Gram.	B. Gram.	C. Gram.
Ca. 'um phosphate	0.8000	0.7000	.....
Cal. ⁻¹ chloride	.....	.....	0.250
Magr . ₁m chloride	0.0200	0.0100	0.0250
Potassium chloride	0.0100	.....	.....
Sodium chloride	.....	0.0100	.....
Iron	0.0185	0.0421	0.0125
Sodium hydrogen phosphate .	.....	.....	2.0000
Aluminum sulphate	0.3504	0.1504	0.1000

gave

	A. Theory. Mgs.	A. Found. Mgs.	B. Theory. Mgs.	B. Found. Mgs.	C. Theory. Mgs.	C. Found. Mgs.
Alumina	56.0	54.5	24.0	24.2	16.0	15.8
	56.0	56.3	24.0	23.9	16.0	15.8

The above-named salts therefore exert no disturbing influence on the accuracy of the final results.

The Effect of Silica.—It is stated by Carnot[1] that "In the presence of silica the precipitate of aluminum phosphate contains a little silica." I have tried to remove this silica by two precipitations but have failed, the plus error equivalent to Al_2O_3 being,

		Mgs.
a	....	1.2
b	....	0.6
c	....	3.3
d	....	2.5

In order to secure correct results, therefore, the silica must be removed from the mixture before the separation of the aluminum phosphate.

The Effect of Sulphates.—Removal of silica being a necessary operation it was determined to make the separation by the well-known method based on the insolubility of silica in sulphuric acid. This method, worked out very carefully by Drown,[2] is a very rapid and accurate process, which is used almost exclusively in the determination of silica in pig-iron. Essentially the same method has been worked out and used by others for the determination of silica in furnace products.

While the separation of silica by this method is all that can be desired it was found to be impossible to completely precipitate the aluminum phosphate with a thiosulphate in the filtrate.

From solutions containing various quantities of the sulphates, phosphates, and chlorides of iron, aluminum, and lime, the following results were obtained :

Experiment.	H_2SO_4 present. Grams.		Alumina. Theory. Mgs.	Found. Mgs.
2	0.100	1 precipitation	39.9	39.8
11	0.20	1 "	79.8	79.6
12	0.20	1 "	....	80.1
19	0.20	1 "	....	80.1
20	0.20	1 "	....	80.8
20*a*	0.10	1 "	23.9	24.2
33*a*	1.250	2 "	39.9	39.6
34*a*	1.250	2 "	....	40.7

[1] Blair's "Chemical Analysis of Iron," p. 188.
[2] *J. Inst. Min. Eng.*, 7, 346.

Experiment.	H$_2$SO$_4$ present. Grams.			Alumina.	
				Theory. Mgs.	Found. Mgs.
50	2.800	2	"	....	38.7
35a	7.500	2	"	19.9	16.8
36a	7.500	2	"	....	18.7
39c	7.500	2	"	39.9	37.9
39d	7.500	2	"	....	37.8
38a	36.000	1	"	31.9	17.2

The presence of more than 1.25 grams of sulphuric acid prevents the complete precipitation of aluminum phosphate, while 2.75 grams give a decided error. The presence of ammonium acetate did not give any better result; see result marked "Experiment 50."

The Effect of Fluorine.—The presence of a fluoride in a solution from which it is attempted to separate aluminum by this method is as disastrous to the results as is the presence of sulphates. From solutions containing phosphates, chloride, and small amounts of sulphates of aluminum, iron, magnesia, lime and soda, and fluoride, the results below are obtained :

			Fluorine present. Mgs.	Alumina.	
				Theory. Mgs.	Found. Mgs.
a	2 precipitation		50	39.9	28.4
b	2 "		50	....	27.4
c	2 "		50	19.9	8.9
d	1 "		250	36.9	31.6
e	2 "		250	....	28.5
f	2 "	1st 10 cc. CH$_3$COONa		....	25.3
g	2 " " "	"		19.9	14.9
h	2 " " "	"		39.9	31.0
i	2 " " "	"		19.9	16.6

In none of the current methods is the presence of fluorine mentioned as a disturbing factor. Several determinations by the acetate method, both single and double precipitation in the presence of dissolved calcium fluoride, showed that it has no effect.

Experiment.	CaF$_2$ present. Mgs.	Alumina.	
		Theory. Mgs.	Found. Mgs.
60a	250	39.9	40.9
60b	250	...	38.1
60c	125	19.9	19.4
60d	125	...	19.8

The Effect of Manganese, with solutions containing :

	Gram.
Aluminum sulphate	0.25
Calcium phosphate	0.5
Ammonium ferrous alum	0.25
Magnesium chloride	0.10
Manganese chloride	0.10

The following data were obtained :

Experiment.	Alumina.		
	Theory. Mgs.		Found. Mgs.
64a	39.9		40.5
64b	....		40.3

The work so far done shows that alumina can be quantitatively separated as phosphate from a hydrochloric acid solution containing aluminum, iron, manganese, lime, magnesium, sodium, and potassium, when only small quantities of sulphate are present, and that the presence of silica in the solution produces a plus error too large to be neglected, and that the presence of large quantities of sulphates or the presence of fluorides prevents the complete precipitation of aluminum phosphate. Therefore, to obtain accurate results, silica and fluorine must be removed while sulphates, not more than the equivalent of 1.25 grams of sulphuric acid, may be present.

The following method for alumina in phosphates is based upon the results of these experiments : Treat 1 gram of substance in a platinum dish with from 5 to 10 cc. hydrofluoric acid, let stand in the cold from two to three hours, heat on the water-bath to complete dryness, add 2 cc. concentrated sulphuric acid, running well around the sides, and heat at a low temperature until the substance no longer flows in the dish. By this process fluorine is completely expelled. Cool and add from 10 to 20 cc. concentrated hydrochloric acid, and warm a few minutes to soften the mass; transfer to a small beaker, and boil until all aluminum compounds are surely dissolved (fifteen to thirty minutes); filter from undissolved residue, if any, washing the filter thoroughly, add 50 cc. 25 per cent. ammonium chloride solution and ammonia until alkaline, then hydrochloric acid until the precipitate just dissolves. Cool, dilute to about 250 cc., and add 50 per

cent. sodium thiosulphate solution, drop by drop, until the solution is colorless, adding in all 20 cc.; cover with a watch-glass, boil half an hour, filter, wash back into the same beaker, and dissolve in boiling hydrochloric acid; reprecipitate exactly as before, after adding 2 cc. of a 10 per cent. ammonium phosphate solution. Wash twenty times with 5 per cent. ammonium nitrate solution, and ignite to constant weight   For the second precipitation ammonium thiosulphate may also be used but it is not strictly necessary.

According to the above method from solutions containing :

	Mgs.
Aluminum sulphate	250
Calcium phosphate	500
Ammonium ferrous alum	250
Silica	100
Calcium fluoride	100
Manganese chloride	100
Magnesium chloride	100

These results recorded below were obtained :

Experiment.	Alumina.	
	Theory. Mgs.	Found. Mgs.
63a	39.9	40.0
63b	....	39.5
63c	....	40.1
63d (contained fluorine)	....	37.8
63e	19.9	19.6
63f	....	20.3
65a	39.9	39.5
65b	....	39.9
66a No. 1 ground S. C. rock	17.0 by acetate method	18.4
66b	....	17.8
67a " 4 " Florida	19.4 " " "	16.3
67b	....	14.3

Move the decimal one place to the left to express percentages.

The phosphoric acid was determined in the aluminum phosphate obtained in Experiment No. 63

	Theory. Mgs.	Found. Mgs.
a	58.2	58.0
b	...	57.6
c	...	57.2

Here, also, the phosphate seems to be the normal, $AlPO_4$, although it was separated in the presence of all substances likely to be found in a natural phosphate, with the exception of silica and fluorine.

The greatest difficulty to be overcome in the execution of this method is the error produced by the presence of fluorine; hence it is necessary to heat the substance for a long time with sulphuric acid to insure the complete removal of fluorine before beginning the separation of the aluminum phosphate.

An attempt to overcome this source of error by adding an alkaline acetate before boiling with thiosulphate gave no better result. In one experiment, however, in which the acetate was added after the boiling, and ten minutes before filtering, all the aluminum phosphate was removed.

The determination of ferric oxide was made as follows : Dissolve 1 gram of substance in 20 cc. sulphuric acid, dilute, filter, washing the filter thoroughly, and if any organic matter is present add a little potassium chlorate and boil until chlorine is expelled. Reduce with zinc, filter, and titrate at once with potassium permanganate solution, 1 cc. of which equals 0.0025 gram ferric oxide.

From solutions used in Experiment 63 I obtained :

	Ferric oxide.	
	Theory. Mgs.	Found. Mgs.
a	51.8	52.5
b	....	52.2
c	....	52.2
d	....	52.2
e	....	51.7
f	....	51.4
No. 1 ground S. C. rock	30.6 by acetate method	29.4
	....	29.3
" 4 " Florida "	14.5	15.4
	....	15.1

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

THE DISTILLATION OF AMMONIA IN THE DETERMINATION OF NITROGEN.

BY FRANCIS GANO BENEDICT.

THE distillation of ammonia in the moist combustion process for determining nitrogen involves the separation of the gaseous ammonia from the alkaline liquid in the distilling flask and the transportation of the gas through a tube into the receiver. While the disengagement of ammonia from a strongly alkaline liquid is readily accomplished by the aid of heat the complete removal of ammonia from the condenser tube is only affected by prolonged boiling to wash the ammonium hydroxide formed out of the tube or by conducting live steam through the tube to vaporize the ammonia which is then driven by the water vapor into the receiver.

The first method is that employed in most laboratories in this country and is designated the "official" method. The second method is that employed in many German laboratories and is here designated the German method.

In the official method the distillation is continued until about 150 cc. of the distillate have been condensed and it is assumed that all the ammonia will have been transferred to the receiver during this operation. The gaseous ammonia coming in contact with the cold water adhering to the inside of the condenser tube dissolves in it forming ammonium hydroxide. The steam generated in the flask condenses in the upper part of the tube and the water formed, slowly runs down, washing out the ammonium hydroxide. It is easily seen that a considerable amount of water would be necessary to insure complete removal of the alkali in this way. Experience has shown that not less than 150 cc. of distillate can safely be relied on to effect this result. This requirement is both expensive and tedious. The operation requires, as a general rule, from forty-five minutes to one hour. Of this time probably not over fifteen to twenty minutes are required to drive all the ammonia out of the liquid, the remaining time being occupied in washing the ammonium hydroxide out of the condenser tube.

According to the German method, the vapors are conducted from the distilling flask through a pipe into the acid, in the receiver with no preliminary cooling, and as a result the contents of the receiver are soon heated to boiling by the latent heat of the steam.   Under these conditions, it has been found that after vigorously boiling for twenty minutes all ammonia has been driven out of the alkaline liquid in the distilling flask.   Inasmuch as the conditions in this flask are the same in both cases it is only correct to assume that in the official method the ammonia is entirely expelled from the liquid in the same length of time.

Under the conditions existing in the distilling flask by the German method probably no ammonium hydroxide is formed in the condenser tube as the whole system is almost immediately brought to the temperature of steam.   Accordingly the gaseous ammonia is carried along mechanically by the water vapor and conducted directly into the receiver.

The great saving in time and gas of this method over the official method is, however, partially offset by the fact that the contents of the receiver at the end of the distillation must be cooled before the titration is made when (as is commonly the case) ammonium hydroxide is used as a standard alkali.   Unless the receiver is well cooled, a loss of ammonia is sure to occur.

A further objection to the German method lies in the fact that a loss of acid is experienced by the passage of so much steam through the hot liquid in the receiver.   This loss should not be neglected in accurate work.

The following modification is, in reality, a combination of the official and the German method, and consists briefly of distilling the liquid into a condenser containing cold water which is allowed to run out a few moments before the end of the distillation that the condenser tubes may become heated.   The ammonia in the tubes is then vaporized and driven into the receiver by a current of live steam.   By this means the rapid removal of ammonium hydroxide in the condenser tubes is effected without unduly heating the contents of the receiver.

The apparatus which has been in constant use in this laboratory for over a year is shown, in part, in the accompanying figure.

The principal feature is the arrangement of the condenser, a galvanized-iron tank 148 cm. long, 38 cm. deep, and 8 cm. wide.

Ten pieces of block tin pipe 4 mm. internal diameter and 70 cm.
long are soldered as usual in the bottom of the tank with ends
about 6 cm. long extending through for connection with the
receiver and bulb.   The upper ends are fastened to one side of
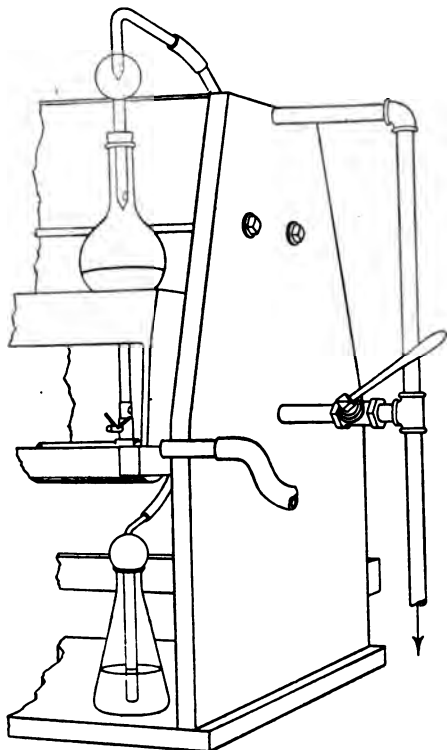
the tank and each is provided with a rubber tube to which a
Hopkins'[1] safety distilling bulb is attached.

At one end of the tank and near the bottom a piece of standard
half inch pipe is inserted, fitted with a valve or gate which is in
turn connected with a ⊤.   An overflow is provided near the top
of the tank and is connected with the ⊤, the lower arm of which
is connected with a sink or drain.   The tank which is filled from
a water tap at the other end is fastened on a stout frame 35 cm.
above the table.   The space below is occupied by the receivers
and bulb tubes used to prevent back suction of liquid.

[1] This Journal, 18, 227.

With the form of apparatus above described the distillation is carried out as follows: The gas is turned on full and the burners are all lighted.[1]   As the liquid in the distilling flask is quite warm from the heat of the dilution of the sulphuric acid and the heat generated by the reaction between the acid and the alkali, the flasks are all vigorously boiling, as a rule, inside of four or five minutes.   When all are boiling the time is noted and at the expiration of fifteen minutes the valve is opened, allowing the water to flow out of the condenser.   As the water runs out the cold water at the bottom is first withdrawn, the layer of hot water at the top gradually settling and warming the block tin pipes.   Just before the layer of hot water begins to flow out the whole condenser tube becomes hot enough to prevent any condensation of water and the live steam blows through the tube into the receiver.   This is allowed to continue till the water in the receiver is warmed slightly, the degree of warming being readily determined by occasionally placing the hand on the receiver.   As soon as a rise in temperature is perceptible the receiver and bulb are disconnected.   This operation requires from four to six minutes after opening the water valve in the apparatus here used.   The contents of the flask are therefore vigorously boiling for from nineteen to twenty-two minutes. Repeated tests have shown that all the ammonia is driven off under these conditions.   With excessive amounts of ammonia, the boiling operation can be prolonged five minutes before opening the valve.   This is seldom necessary, however.   Ordinarily, twenty-five to thirty minutes from the lighting of the gas under the flasks to the removal of the receivers suffice to complete the distillation.   The titrations can be made immediately.   .

The length of time necessary to draw off the water in the condenser tank to such a level as to cause live steam to blow through the block tin pipes, is determined by the sizes of the waste pipe and the condenser.   With very little experience, it is not difficult to determine how long after boiling the valve should be opened to produce the desired effect at the end of twenty minutes.

The condenser tank here described was not constructed pri-

[1] The use of Jena glass digestion as well as distillation flasks is strongly recommended.   With such flasks the full free flame may be employed with impunity.   The distillation flasks contain approximately 500 cc. and are about half filled with the alkaline liquid.

marily for this method of distillation. It could undoubtedly be diminished very materially in size with equally satisfactory results.

Obviously the principle is capable of application to numerous forms of condensers. It is only necessary to observe that the flasks are vigorously boiling for at least nineteen or twenty minutes. In a local laboratory the principle has been easily applied to a two-tube condenser constructed out of an old ether can. This apparatus has also given excellent satisfaction for over a year.

MIDDLETOWN, CONNECTICUT.

THE GLUTEN CONSTITUENTS OF WHEAT AND FLOUR AND THEIR RELATION TO BREAD-MAKING QUALITIES.

BY H. A. GUESS.

DURING the last eighteen months the writer has been pursuing some investigations in the chemical factors which determine bread-making qualities of wheats and flours, and the notes here submitted, representing some results of the work, are offered as contributions to the chemical literature of an as yet rather neglected subject.

As aids in the work advantage was taken of published notes by other investigators, acknowledgments being more particularly due to the papers of M. E. Fleurent,[1] and of Mr. G. L. Teller.[2]

The result of considerable preliminary work in the estimation of the proteids of both wheats and flours, and subsequent comparisons with results of milling and baking tests, led the writer to confine his attention more particularly to the determination of the gluten constituents gliadin and glutenin, as being apparently the chief determining factors in bread-making qualities.

In the estimation of the gliadin and glutenin, five nitrogenous bodies were considered as being present in the samples,—gliadin,

[1] "Sur la composition immédiate du gluten des cereals."—*Compt. rend.*, 123, 327. "Determination of Gluten in Wheat Flour."—Third Congress of Applied Chemistry. Vienna, August, 1898.

[2] "Concerning Wheat and its Mill Products: A report of progress of investigations in the chemistry of wheat."—Arkansas Expt. Station, 1898.

glutenin, edestin, leucosin, and the amides. For the separation of the gliadin, alcohol of 0.90 sp. gr. was used, and after deducting the nitrogen of the amides present, the balance of the nitrogen in the alcohol extract, was calculated as gliadin.[1]

The nitrogen of the amides was determined on a separate sample, by extraction with one per cent. salt solution, precipitating all proteids with phosphotungstic acid, and determination of the amide nitrogen in the filtrate.

The edestin and leucosin were separated from the residue from the alcohol extraction, by extraction with one per cent. salt solution, and the nitrogen remaining in the final residue, calculated as glutenin. By making the 1 per cent. salt solution extraction on the residue from the alcohol extract, any uncertainty from partial solubility of gliadin, or allied proteid bodies, in salt solution, was avoided.[2]

The *modus operandi* of the analysis, was as follows :

a. Five grams of the finely ground wheat meal or flour, placed in a 250 cc. flask, 1 per cent. salt solution added from a pipette, at sufficient pressure to prevent any tendency to clot ; flask filled to the mark, shaken at intervals for one hour, and let settle for two hours ; decanted through a filter, duplicate portions of 100 cc. each of the clear supernatant liquid withdrawn, the proteids precipitated with a few cubic centimeters of 10 per cent. solution of phosphotungstic acid, the precipitate allowed to settle, 50 cc. of the clear filtrate evaporated with sulphuric acid, and the amide nitrogen determined.

b. One gram of sample put in a 500 cc. Kjeldahl flask with 100 cc. alcohol of 0.90 sp. gr., shaken to thoroughly mix, placed on a water-bath, and maintained at a temperature slightly below the boiling-point of the alcohol mixture ; agitated every ten minutes for one hour, allowed to settle for one hour and decanted into a similar flask, being careful to not carry decantation close enough to cause any turbidity to appear in the decanted filtrate ; 25 cc. fresh hot alcohol added, allowed to settle twenty minutes, decanted, and the operation repeated three times. In the extract, the alcohol is distilled off, and the nitro-

[1] *Am. Chem. J.*, 15, 441.
[2] *Ibid.*, 392 *et seq.*

gen in the residue determined, the amide nitrogen (*a*) subtracted, and the balance calculated as gliadin (N × 5.7).

c. To the residue from the alcohol extraction, after cooling, 250 cc. of 1 per cent. salt solution are added ; it is allowed to settle for one hour, and decanted through a filter ; 250 cc. fresh salt solution are added, shaken at intervals for one hour and allowed to settle for two hours, decanting through the same filter ; the filter and contents are added to the residue in the flask, and nitrogen determined and calculated to glutenin.

Following are results of some determinations made in this way on wheats from different elevator points, throughout the Canadian Northwest, giving the locality, the buyer's regular grading mark, the percentages of gliadin and glutenin respectively ; the ratio of same, and a composite factor representing this ratio × the total percentage of gluten (gliadin and glutenin) present. Also of the same determinations made at regular intervals on the flours produced from these wheats, by one of the largest milling companies in Canada. Analyses of the different ' break' products of the mill were also similarly made, but are not here included.

This ratio of gliadin to glutenin has been used tentatively, as an index of the gluten quality. So far as the writer has been enabled to have this index checked by actual baking tests on the flour produced, it was found that the elastic quality of the gluten was improved in proportion as the ratio of gliadin to glutenin increased, and as yet no limit has been found beyond which further increase of gliadin ratio rendered the gluten inelastic or sticky.

Manifestly, if this ratio of gliadin to glutenin be a true index of the quality of the gluten, the factor of quantity must also be taken account of in estimating the true gluten value of a wheat or flour, the value being the total number of units of gluten present × the value per unit. Need was felt, in the work, for a factor to indicate this gluten value, so as to be of use commercially, in grading wheats and flours, and in the lists following this gluten value is in each case calculated out as a composite factor made up of the percentage of gluten × ratio of gliadin to glutenin (quality index).

CANADIAN NORTHWEST WHEATS.

Locality.	Buyer's grade.[1]	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of Gliadin to Glutenin.	Composite factor. Gluten ratio. Per cent.
Reston	2 H	7.32	4.43	1.65	19.38
Plum Coulee ..	1 N	5.4	3.61	1.49	13.42
Carman	1 H	7.77	3.30	2.34	25.90
Holland	2 H	5.73	4.0	1.43	13.91
Lauder	2 H	7.18	4.67	1.53	.18.13
Virden (damp)	1 H	5.19	4.93	1.05	10.62
Lauder '97	1 H	8.39	4.61	1.8	23.4
Franklin	1 N	6.14	4.53	1.35	14.40
Hartney	1 H	5.43	4.24	1.2	11.6
Dom. City	2 N	5.15	3.71	1.38	12.22
McDonald	1 N	5.51	5.08	1.08	11.43
Manitou	2 N	4.57	5.91	0.7	7.33
Altonia	1 H	6.53	4.25	1.54	16.60
Reston	1 H	7.7	4.88	1.57	19.75
Treesbank	1 H	7.36	5.0	1.47	18.16
Douglass	1 H	7.7	4.4	1.77	21.41
Qu'appelle	1 H	7.86	4.16	1.9	22.84
Souris	1 H	7.01	5.10	1.37	16.59
Indian Head ..	1 H	7.98	4.92	1.62	20.89
Sintaluta	1 H	8.14	5.2	1.56	20.81
Whitewater ...	1 H	6.12	5.44	1.12	12.95
Boissevain	1 H	6.46	4.84	1.33	15.02
Stocton	1 H	6.62	4.40	1.5	16.53
Rosenfeldt	1 H	5.14	5.04	1.0	10.18
Ninga	2 H	5.59	5.0	1.11	11.97
McGregor	1 N	6.02	4.88	1.23	13.40
Neepawa	1 N	4.76	4.64	1.0	9.4
Portage	..	6.7	4.92	1.36	15.66
Portage (damp)	..	6.4	6.08	1.05	13.10
Elkhorn	1 H	7.06	5.2	1.35	16.55
Thornhill	1 N	6.5	4.4	1.47	16.02
Fleming	1 H	7.50	5.09	1.47	18.52
Griswald	1 H	7.50	5.64	1.33	17.48
Mileta	1 H	8.18	5.04	1.6	21.15
Bagat	2 H	7.34	5.0,	1.47	18.13
Alemeda	1 H	8.29	4.45	1.86	23.69
Stocton	L White Fife	6.6	4.7	1.4	15.82
Sintaluta	1 H	9.21	4.60	2.1	27.62
Methven	1 H	8.52	5.0	1.7	22.98
Elkhorn(damp)	..	8.13	4.64	1.75	22.34
Carroll	..	7.58	5.30	1.43	18.42
Indian Head ...	1 H	7.88	4.77	1.65	20.87

[1] Grades in descending. 1 Hard ; 2 Hard ; 1 Northern ; 2 Northern.

Locality.	Buyer's grade.[1]	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of Gliadin to Glutenin.	Composite factor. Gluten ratio. Per cent.
Arden	1 N	5.07	5.49	0.92	9.71
Treesbank.....	1 H	8.76	4.82	1.81	24.57
Alemeda	1 White Fife	8.85	4.6	1.92	25.82
McGregor	2 H	6.44	4.36	1.47	15.87
Dauphin	1 N	4.25	4.25	1.0	8.5
Morden	1 N	3.65	3.65	1.0	7.3
Gretna	1 N	3.8	3.7	1.0	7.5
McDonald.....	2 H	5.8	4.0	1.45	13.21
Carberry	1 N	5.7	3.7	1.53	14.38
Moosomin.....	1 H	7.65	4.0	1.9	22.13
Treesbank	1 H	7.87	4.3	1.83	22.47
Neepawa	1 N	6.65	4.2	1.57	17.03
Indian Head ..	1 H	6.35	4.1	1.51	16.48
Carroll........	1 H	6.7	4.1	1.63	17.60
Elva	2 H	7.6	3.95	1.92	22.17
Winkler	1 N	6.0	3.5	1.71	16.24
Altonia........	1 N	7.5	4.1	1.82	21.11
Dom. City.....	2 N	5.4	3.7	1.46	13.28
Elkhorn(damp) ..		6.5	4.0	1.65	18.00
Elva	2 H	8.37	4.3	1.94	24.58
Reston	2 H	8.0	4.5	1.78	22.25
Douglass (damp) ..		6.65	4.2	1.58	17.13
Sintaluta......	1 H	7.77	4.5	1.73	21.2
Boissevain	1 H	7.3	4.4	1.65	19.3
Qu'appelle	1 H	8.58	4.2	2.904	26.0
Manitou.......	2 Spring	4.0	4.2	0.95	7.78
Bagat	1 N	3.7	4.0	0.93	7.20
McGregor	1 N	4.65	4.10	1.1	9.62
Thornhill	1 N	5.4	4.2	1.3	12.48
Hamiota	1 H	7.15	4.6	1.54	18.10
Hartney	1 H	7.8	4.0	1.95	23.0
Treesbank	..	8.37	4.0	2.09	25.85
Indian head ...	..	7.51	4.1	1.83	21.24
Carman	..	7.77	3.6	2.14	24.18
Douglass	..	7.8	3.8	2.0	23.2
Bagat..........	..	7.0	4.2	1.66	18.59
Holland	..	6.1	4.4	1.4	14.7
Methven	..	8.1	4.0	2.02	24.44

[1] Grades, in descending order : 1 Hard ; 2 Hard ; 1 Northern ; 2 Northern.

CANADIAN NORTHWEST AND OTHER FLOURS.

Name of flour.	Grade.[1]	Gliadin. Per cent	Glutenin. Per cent.	Ratio of gliadin to glutenin.	Composite factor. Per cent. gluten × ratio.
Keewatin	Patent	8.13	2.24	3.62	37.54
"	Baker's	8.47	3.90	2.17	26.84
"	Algoma	7.98	4.55	1.75	21.92
"	Glenwood	7.2	5.53	1.3	16.54
Portage	Patent	8.4	2.1	4.0	42.00
"	Baker's	8.65	2.6	3.32	37.25
"	Algoma	8.2	3.2	2.59	29.78
"	Glenwood	8.0	4.7	1.7	21.69
Keewatin	Patent	8.9	1.60	5.56	58.38
"	Baker's	8.14	3.52	2.3	26.81
"	Algoma	7.46	4.80	1.6	19.61
"	Glenwood	6.90	5.90	1.2	15.38
Austria-Hungary (best)		9.38	2.80	3.35	40.80
Keewatin	Patent	8.25	2.0	4.12	42.23
"	Baker's	9.06	2.25	4.02	45.46
"	Algoma	8.63	3.24	2.66	31.57
"	Patent	9.0	1.9	4.73	51.55
"	Baker's	8.65	3.2	2.7	32.0
"	Algoma	8.5	3.8	2.23	27.42
"	Glenwood	8.1	4.9	1.65	21.45
"	Patent	7.95	2.85	2.78	30.02
"	Baker's	8.1	3.1	2.61	29.23
Ogilvie	Patent	8.04	2.92	2.76	30.24
"	Baker's	7.4	3.6	2.05	22.55

At the present stage of progress in these investigations, it cannot be stated that these ratios, or the calculated factors, are true indices of the bread-making qualities and values of the different wheats and flours, but it is certain that there is a direct and very intimate connection between the same.

The subject is one worthy of attention by industrial chemists, and it is quite possible that in time the buying, mixing, and milling of wheats may come under as definite chemical control as are, at present, similar operations, with respect to the smelting of ores.

LABORATORY OF THE OTTAWA GOLD MILLING AND
MINING CO., KEEWATIN, ONTARIO, March 6, 1900.

[1] Grades in descending scale : Patent, Baker's, Algoma, Glenwood.

LIME AND SULPHURIC ACID BY THE PHOTOMETRIC METHOD.

BY J. I. D. HINDS.

IN this Journal, **18**, 661, I gave the results of some investigations looking to the rapid determination of lime and sulphuric acid by means of the opacity of the precipitates produced in the usual way. Since then I have had occasion to make frequent tests of the accuracy of the method and am able to give some interesting results.

The only apparatus needed is the photometric cylinder made of glass. It is 3.5 centimeters wide and 20 centimeters high, and is graduated in centimeters and millimeters from the inside of the bottom for the convenient reading of the depth of the liquid in the cylinder. It is used with an ordinary sperm or wax candle. The cylinder is held over the lighted candle and the water containing the precipitate is poured into the cylinder until the image of the flame just disappears. The depth is read and the per cent. is calculated from the equation or read from a table. The lime is precipitated with solid calcium oxalate and the sulphuric acid with solid barium chloride. The equations used are as follows :

$$\text{For CaCO}_3, y = \frac{0.0642}{x - 0.3}; \qquad \text{For CaO}, y = \frac{0.0360}{x - 0.3};$$

$$\text{For H}_2\text{SO}_4, y = \frac{0.0590}{x}; \qquad \text{For SO}_3, y = \frac{0.0482}{x};$$

in which x is the reading of the cylinder and y the per cent. sought. For the details of the method, see the article above referred to. A table computed from these equations is appended to this article.

Near the university building in Lebanon is a bored well yielding a limestone water, analysis of which shows that it contains among other things

Calcium carbonate about	16.00 parts in	100,000
Magnesium " "	13.00 " "	100,000
Magnesium sulphate "	16.00 " "	100,000
Total solids	60.80 " "	100,000

I made a series of photometric and gravimetric determinations of the lime and sulphuric acid in this water from day to day, with the following results :

Calcium carbonate—parts in 100,000.

	1.	2.	3.	4.	5.	6.	7.
Photometric..........	16.5	15.7	15.7	16.5	15.7	22.2	19.5
Gravimetric..........	16.4	16.0	15.5	16.0	15.5	22.4	19.0
Difference...........	0.1	0.3	0.2	0.5	0.2	0.2	0.5

Sulphuric acid—parts in 100,000.

	1.	2.	3.	4.	5.
Photometric...............	13.1	11.8	5.7	7.9	4.9
Gravimetric...............	13.2	11.4	5.4	7.2	4.7
Difference................	0.1	0.4	0.3	0.7	0.2

These differences, omitting the decimal point, mean parts in a million of the water and are a reasonably small fraction of the total amount present. For sanitary and technical purposes the photometric determinations are just as good as those made in the regular way. When we consider that one of these determinations can be made in five minutes and that the method is adapted to many other substances, it seems to be worthy of the attention and careful investigation of chemists. It is much more accurate than many of the approximate methods now in use and requires no previous preparation in the way of standard solutions.

I have found the method practicable in the determination of the lime in carbonates. I give one example. A sample of clayey limestone containing 16.14 per cent. of calcium carbonate gave by this method 16.46 per cent. The determination was made as follows: Dissolved 0.1081 gram of the limestone in hydrochloric acid with a few drops of nitric acid, evaporated to dryness in a porcelain dish over a free flame, added water with a little hydrochloric acid, filtered, neutralized with ammonia, made up to 150 cc., then tested in the usual way. The reading in the cylinder was 6.0 cm. Substituting this for x in the equation we find the solution to contain 0.0112 per cent. of calcium carbonate. The calculation is then made as follows :

100 cc. contain 0.0112 gram $CaCO_3$.
150 "   "   0.0178 "   "

0.1081 gram of the sample contains 0.0178 gram $CaCO_3$, or

16.46 per cent. The whole operation can be performed within a half hour.

The determination of sulphuric acid in urine is very easy and rapid. Five or ten cc. of the urine are measured from a burette or pipette, made slightly acid with hydrochloric acid, and diluted to 100 cc. Barium chloride is added and the reading taken. Two trials with a urine diluted from 10 to 100 cc. gave the same reading; *viz.*, 3.0 cm. This corresponds to 0.0197 per cent. H_2SO_4. Multiplying by 10 we have 0.197 as the per cent. of H_2SO_4 in the urine.

To save the trouble and labor of computation I have prepared the accompanying table from which the percentages can be directly taken as soon as the reading is made.

TABLE FOR PHOTOMETRIC DETERMINATION OF LIME AND SULPHURIC ACID.

y equals the per cent. desired, and x is the reading of cylinder in centimeters. For parts in 100,000 remove the decimal point three places to the right.

x.	Per cent. $CaCO_3$. $y = \dfrac{0.0642}{x - 0.3}$.	Per cent. CaO. $y = \dfrac{0.0360}{x - 0.3}$.	Per cent. H_2SO_4. $y = \dfrac{0.0590}{x}$.	Per cent. SO_3. $y = \dfrac{0.0482}{x}$.
1.0	0.0917	0.0514	0.0590	0.0482
1.1	0.0802	0.0450	0.0536	0.0438
1.2	0.0713	0.0400	0.0492	0.0402
1.3	0.0642	0.0360	0.0454	0.0371
1.4	0.0583	0.0327	0.0421	0.0344
1.5	0.0534	0.0300	0.0393	0.0322
1.6	0.0494	0.0277	0.0370	0.0301
1.7	0.0456	0.0257	0.0347	0.0283
1.8	0.0428	0.0240	0.0328	0.0268
1.9	0.0401	0.0225	0.0311	0.0254
2.0	0.0377	0.0212	0.0295	0.0241
2.1	0.0356	0.02C1	0.0281	0.0230
2.2	0.0338	0.0190	0.0268	0.0219
2.3	0.0321	0.0180	0.0257	0.0210
2.4	0.0306	0.0172	0.0246	0.0201
2.5	0.0292	0.0164	0.0236	0.0193
2.6	0.0279	0.0156	0.0227	0.0185
2.7	0.0268	0.0150	0.0218	0.0179
2.8	0.0257	0.0144	0.0211	0.0172
2.9	0.0247	0.0138	0.0203	0.0166
3.0	0.0238	0.0133	0.0197	0.0161
3.1	0.0229	0.0129	0.0190	0.0156
3.2	0.0221	0.0124	0.0184	0.0151

x.	Per cent. $CaCO_3$. $y = \dfrac{0.0642}{x-0.3}$.	Per cent. CaO. $y = \dfrac{0.0360}{x-0.3}$.	Per cent. H_2SO_4. $y = \dfrac{0.0590}{x}$.	Per cent. SO_3. $y = \dfrac{0.0482}{x}$.
3.3	0.0214	0.0120	0.0179	0.0146
3.4	0.0207	0.0116	0.0174	0.0142
3.5	0.0201	0.0112	0.0169	0.0138
3.6	0.0195	0.0109	0.0164	0.0134
3.7	0.0189	0.0106	0.0159	0.0130
3.8	0.0183	0.0103	0.0155	0.0127
3.9	0.0178	0.0100	0.0151	0.0124
4.0	0.0173	0.0097	0.0147	0.0121
4.1	0.0169	0.00947	0.0144	0.0118
4.2	0.0165	0.00923	0.0141	0.0115
4.3	0.0161	0.00900	0.0137	0.0112
4.4	0.0157	0.00878	0.0134	0.0110
4.5	0.0153	0.00857	0.0131	0.0107
4.6	0.0149	0.00837	0.0128	0.0105
4.7	0.0146	0.00818	0.0125	0.0103
4.8	0.0143	0.00800	0.0123	0.0101
4.9	0.0140	0.00782	0.0120	0.00983
5.0	0.0137	0.00766	0.0118	0.00964
5.1	0.0134	0.00750	0.0116	0.00945
5.2	0.0131	0.00735	0.0113	0.00927
5.3	0.0128	0.00720	0.0111	0.00909
5.4	0.0126	0.00706	0.0109	0.00992
5.5	0.0123	0.00692	0.0107	0.00876
5.6	0.0121	0.00679	0.0105	0.00861
5.7	0.0119	0.00667	0.0104	0.00845
5.8	0.0117	0.00654	0.0102	0.00831
5.9	0.0115	0.00643	0.0100	0.00817
6.0	0.0113	0.00632	0.00983	0.00804
6.1	0.0111	0.00621	0.00967	0.00790
6.2	0.0109	0.00610	0.00952	0.00777
6.3	0.0107	0.00600	0.00937	0.00765
6.4	0.0105	0.00590	0.00922	0.00753
6.5	0.0104	0.00580	0.00908	0.00742
6.6	0.0102	0.00571	0.00894	0.00730
6.7	0.01003	0.00562	0.00881	0.00719
6.8	.	0.00554	0.00868	0.00709
6.9	0. ⁖	0.00545	0.00855	0.00698
7.0	0.00958	0.00537	0.00843	0.00689
7.1	0.00944	0.00529	0.00831	0.00679
7.2	0.00930	0.00522	0.00820	0.00669
7.3	0.00917	0.00514	0.00808	0.00660
7.4	0.00904	0.00507	0.00797	0.00651
7.5	0.00892	0.00500	0.00787	0.00642
7.6	0.00879	0.00493	0.00776	0.00634

x	Per cent. $CaCO_3$. $y = \dfrac{0.0642}{x - 0.3}$.	Per cent. CaO. $y = \dfrac{0.0360}{x - 0.3}$.	Per cent. H_2SO_4. $y = \dfrac{0.0590}{x}$.	Per cent. SO_3. $y = \dfrac{0.0482}{x}$.
7.7	0.00867	0.00486	0.00766	0.00626
7.8	0.00856	0.00480	0.00756	0.00618
7.9	0.00845	0.00474	0.00747	0.00610
8.0	0.00834	0.00468	0.00737	0.00602
8.1	0.00823	0.00462	0.00728	0.00595
8.2	0.00813	0.00456	0.00720	0.00588
8.3	0.00802	0.00450	0.00711	0.00581
8.4	0.00792	0.00444	0.00702	0.00574
8.5	0.00783	0.00439	0.00694	0.00567
8.6	0.00773	0.00434	0.00686	0.00560
8.7	0.00764	0.00429	0.00678	0.00554
8.8	0.00755	0.00424	0.00670	0.00548
8.9	0.00746	0.00419	0.00663	0.00541
9.0	0.00738	0.00414	0.00655	0.00536
9.1	0.00730	0.00409	0.00648	0.00530
9.2	0.00721	0.00404	0.00641	0.00524
9.3	0.00713	0.00400	0.00634	0.00518
9.4	0.00705	0.00396	0.00628	0.00513
9.5	0.00698	0.00391	0.00621	0.00507
9.6	0.00690	0.00387	0.00615	0.00502
9.7	0.00683	0.00383	0.00608	0.00497
9.8	0.00676	0.00379	0.00602	0.00492
9.9	0.00669	0.00375	0.00596	0.00487
10.0	0.00662	0.00371	0.00590	0.00482
10.1	0.00655	0.00367	0.00584	0.00477
10.2	0.00648	0.00364	0.00578	0.00473
10.3	0.00642	0.00360	0.00573	0.00468
10.4	0.00636	0.00357	0.00567	0.00463
10.5	0.00629	0.00353	0.00562	0.00459
10.6	0.00623	0.00350	0.00557	0.00455
10.7	0.00617	0.00346	0.00551	0.00451
10.8	0.00611	0.00343	0.00546	0.00447
10.9	0.00606	0.00340	0.00541	0.00442
11.0	0.00600	0.00336	0.00536	0.00438
11.1	0.00594	0.00333	0.00532	0.00434
11.2	0.00589	0.00330	0.00528	0.00430
11.3	0.00584	0.00327	0.00523	0.00426
11.4	0.00578	0.00324	0.00518	0.00423
11.5	0.00573	0.00321	0.00513	0.00419
11.6	0.00568	0.00318	0.00508	0.00415
11.7	0.00563	0.00316	0.00504	0.00412
11.8	0.00558	0.00313	0.00500	0.00408
11.9	0.00555	0.00310	0.00496	0.00405
12.0	0.00548	0.00308	0.00492	0.00401

$x.$	Per cent. $CaCO_3$. $y = \dfrac{0.0642}{x-0.3}$.	Per cent. CaO. $y = \dfrac{0.0360}{x-0.3}$.	Per cent. H_2SO_4. $y = \dfrac{0.0590}{x}$.	Per cent. SO_3. $y = \dfrac{0.0482}{x}$.
12.1	0.00543	0.00305	0.00488	0.00398
12.2	0.00539	0.00303	0.00484	0.00395
12.3	0.00535	0.00300	0.00480	0.00392
12.4	0.00531	0.00298	0.00476	0.00389
12.5	0.00526	0.00295	0.00472	0.00386
12.6	0.00522	0.00293	0.00468	0.00383
12.7	0.00517	0.00290	0.00465	0.00380
12.8	0.00513	0.00288	0.00461	0.00377
12.9	0.00509	0.00285	0.00457	0.00374
13.0	0.00505	0.00283	0.00454	0.00371
13.2	0.00498	0.00279	0.00447	0.00364
13.4	0.00490	0.00275	0.00440	0.00359
13.6	0.00483	0.00271	0.00434	0.00354
13.8	0.00476	0.00267	0.00427	0.00349
14.0	0.00469	0.00263	0.00421	0.00344
14.2	0.00462	0.00259	0.00415	0.00339
14.4	0.00455	0.00255	0.00410	0.00335
14.6	0.00449	0.00251	0.00404	0.00330
14.8	0.00443	0.00248	0.00399	0.00326
15.0	0.00437	0.00245	0.00393	0.00321
15.5	0.00422	0.00237	0.00381	0.00311
16.0	0.00409	0.00229	0.00369	0.00301
16.5	0.00396	0.00222	0.00358	0.00292
17.0	0.00384	0.00216	0.00347	0.00284
17.5	0.00373	0.00209	0.00337	0.00276
18.0	0.00363	0.00203	0.00328	0.00268
18.5	0.00353	0.00198	0.00319	0.00261
19.0	0.00343	0.00192	0.00311	0.00254
19.5	0.00334	0.00187	0.00303	0.00247
20.0	0.00326	0.00183	0.00295	0.00241

UNIVERSITY OF NASHVILLE.

UPON BISMUTH COBALTICYANIDE.

BY J. A. MATHEWS.

IN a recent article entitled "A Preliminary Study of the Cobalt-icyanides,"[1] by E. H. Miller and myself, mention was made of bismuth cobalticyanide. It was stated that "the original pre-cipitate seems to be a normal cobalticyanide, but it has not been analyzed and no mention of such a compound is found in the

[1] This Journal, 22, 65 (1900).

literature.'' It was further stated that as lead cobalticyanide is exceedingly soluble in water, there might be a possibility of effecting a separation of bismuth from lead in pig-leads by the use of potassium cobalticyanide. I have analyzed the cobalticyanide of bismuth, noted carefully its properties, and determined the most favorable conditions for its precipitation. The results have not been favorable to its use in the analysis of pig-leads but it may still be found useful in the analysis of lead-bismuth alloys, ''fusible metals'' such as Wood's alloy, etc.

The precipitate of bismuth cobalticyanide is crystalline, settles and filters well, and contains more or less water which is not completely given up below 165° C. The anhydrous compound has the formula $BiCo(CN)_6$. The theoretical percentage of bismuth for this compound is 49.17. The average of three determinations gave 49.05 per cent. bismuth. When freshly precipitated and before filtering; the precipitate appears white but on the filter it has a slight greenish tint. During the process of dehydrating the color becomes blue, getting darker as the temperature rises; then upon exposure to the air it reabsorbs water rapidly and the color becomes pink. This behavior seems to indicate some decomposition of the cobalticyanide radical at the temperature required for complete dehydration, and this view is strengthened by the fact that different samples exhibit differences of tint and that, in general, after exposing the anhydrous samples to the air, the depth of the pink tint is proportional to the depth of blue in the sample exposed.

A sample of bismuth cobalticyanide dried below 100° C. and exposed to the air for one week, lost by subsequent heating to 162° C., 19.5 per cent. Two portions dried to constant weight at 100° C. lost, by heating to 165° C., 4.35 per cent. and 4.24 per cent. respectively, corresponding to one molecule of water. The samples upon exposure to the air reabsorbed about 16.25 per cent. of water, the actual percentage fluctuating slightly from day to day.

Completeness of the Precipitation.—By means of several series of experiments in which bismuth solutions were precipitated by potassium cobalticyanide, it was found that below a concentration of 0.0079 gram of bismuth per cubic centimeter the precipitate was under no conditions complete and that at ten times

that dilution no precipitate was produced even on long standing. By varying the ratio of bismuth to potassium cobalticyanide, it was shown that a decided excess of the latter was beneficial. The precipitation is found to be more complete if acetic acid is present. Boiling assists in the precipitation of very dilute solutions, but a solution so dilute that no precipitate forms in the cold is never completely precipitated by heating. The solubility of the precipitate does not vary much with change of temperature, and when once formed is not soluble in a quantity of water which would have prevented its formation in the beginning.

The following tables, with the remarks accompanying each, show the influence of different conditions upon the completeness of precipitation. A solution containing 0.0794 gram of bismuth per cubic centimeter in nitric acid was used in all cases.

I. VARYING RATIO OF $Bi(NO_3)_3$ TO $K_3Co(CN)_6$.

	Temperature.	$Bi(NO_3)_3$. cc.	Half-normal $K_3Co(CN)_6$. cc.
1	cold	5	15
2	"	3	15
3	"	1	15
4	hot	5	15
5	"	3	15
6	"	1	15

All filtrates showed a trace of bismuth with $(NH_4)_2S$: Greater in 4, 5, and 6, than in 1, 2, and 3; deepest in 1 and 4; least in 3 and 6, respectively. The insolubility is therefore increased by an excess of $K_3Co(CN)_6$.

II. VARYING VOLUME. RATIO OF $Bi(NO_3)_3 : K_3Co(CN)_6$ CONSTANT.

	$Bi(NO_3)_3$. cc.	H_2O. cc.	$K_3Co(CN)_6$. cc.
1	5	5	15
2	3	7	9
3	1	9 ($+ \overline{HA}$)	3 also,
[4	1	9	6]

Number 3 is very incomplete. Filtrate gave large precipitate with ammonium carbonate. 1, 2, and 4 showed only a trace of bismuth with $(NH_4)_2S$. Comparison of 3 and 4 shows the effect of increasing the amount of $K_3Co(CN)_6$.

III. CONSTANT VOLUME.

	Bi(NO₃)₃. cc.	H₂O(+HA̅). cc.	K₃Co(CN)₆. cc.
1	5	5	15
2	3	12	10
3	1	19	5
4	1	21	3

In 1, 2, and 3 the ratio of $K_3Co(CN)_6$ to $Bi(NO_3)_3$ increases with the dilution. Filtrate from 3 contained 10 per cent. of the bismuth; filtrate from 4 contained 57 per cent. of the bismuth. In 1 and 2, the filtrates showed a trace of bismuth with $(NH_4)_2S$, greater in 2 than in 1, showing that the completeness of the precipitation increases with the concentration.

A RAPID METHOD FOR THE DETERMINATION OF CARBON IN IRON OR STEEL BY COMBUSTION.

BY GEO. WM. SARGENT.

THE part taken by the carbon in determining the utility of steel or iron, especially the effect of slight changes in the quantity, impresses one with the need of exercising the greatest care that its estimation may be accurately made, and yet the large number of determinations required in a limited time calls for greater speed in their accomplishment.

The color method of Eggertz is probably the most rapid, but its application is so limited that it is scarcely used outside of regular furnace work where straight steels only are encountered, and the steel has undergone the same treatment, consequently the carbon is present in always the same condition. The advent of alloys of nickel, chromium, tungsten, molybdenum, titanium, etc., with iron, forces even the furnace chemist back to the most reliable method,—that of the combustion, in oxygen, of the carbon residue from the solution of the drillings. During the past three months the results obtained in this laboratory, by this method somewhat modified, have been so eminently gratifying with regard to accuracy, rapidity, and simplicity of the apparatus used, that I believe it worthy the attention of other chemists.

The apparatus as shown by the accompanying cut consists of, beginning on the right, a small copper or platinum spiral, water-jacketed at each end to prevent the burning of the rubber con-

nections, and suspended in a copper cyl-
inder over a burner; a Geissler potash
bulb, followed by an empty "safety"
tube, then the porcelain tube resting in a
three-burner combustion furnace; a glass
tube filled with coarse, wet sand; a cop-
per tube filled with copper oxide and
also water-jacketed at each end; a tin can
containing a copper worm; then a 6-inch
calcium chloride tube; the weighed pot-
ash bulb and its calcium chloride tube;
and finally the guard.
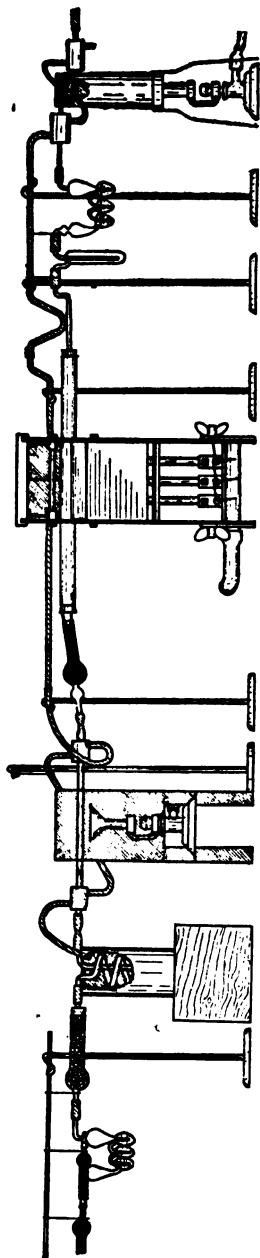
It will be best to describe in detail each
portion of the apparatus and its function.

The spiral is made from a platinum
tube 17 inches long and $\frac{5}{32}$ inch in diam-
eter. This gives four close coils $\frac{3}{4}$ inch
in diameter and leaves 4 inches extend
on either side. The water-jackets are
two pieces of $\frac{1}{2}$ inch copper tubing $1\frac{1}{2}$
inches long, closed at the ends by rivet
burrs, carefully soldered and containing
an outlet and an inlet, the outlet of the
one being connected to the inlet of the
other by a $\frac{1}{4}$ inch copper tube bent around
the support. The latter is a $1\frac{1}{2}$ inch
copper tube with $\frac{1}{16}$ inch walls, 6 inches
long, resting on three legs sufficiently
long to bring the spiral the proper dis-
tance from the burner. A two-way cock
leads the oxygen or air from the tanks
to the spiral where any hydrocarbons
are burned. The resulting carbon diox-
ide is caught in the Geissler potash bulb
to which the spiral is connected by rub-
ber tubing, thence the purified oxygen
or air passes through the empty tube
which is used to catch any potassium hy-
droxide from the Geissler bulb, into the
combustion tube. Both the potash

bulb and the "safety" are suspended from the small cop-
per pipe conveying the water from the outlet of the second water-
jacket to the first jacket on the copper oxide tube. The
combustion tube is a $\frac{5}{8}$ inch glazed porcelain tube 16 inches long,
5 inches of which extend on either side of the combustion fur-
nace. The curved piece of fire-brick protects the tube from
direct contact with the flames of the furnace. The latter is 5
inches long, having but 3 burners and was made from an old
10-burner furnace. To prevent the boat holding the carbon
from being pushed into the combustion tube beyond the heated
portion, a piece of clay pipe stem is placed at one end. The gases
from the combustion tube pass through the coarse, wet sand
loosely packed in a $\frac{1}{2}$ inch glass tube 6 inches long and held in
place by two small disks of copper gauze placed at either end.
This moist sand and the copper disks effectually hold any hydro-
chloric acid or chlorine that the gases may contain. The cop-
per oxide tube is a straight piece of copper $\frac{3}{8}$ inch in diameter, 1
foot long, water-jacketed at each end, the water flowing from the
outlet of the first jacket to the second, and thence into the tin
can containing the worm. The copper oxide tube rests on a sup-
port of sheet tin, bent as shown in the cut, and slit at each side
and at the bottom of the back, the two side openings supporting
the copper tube, while the one in the back allows the gas pipe
to enter to the burner, which has a spreader so that the copper
oxide is heated for a distance of at least 3 inches. The worm
consists of 3 very loose coils of $\frac{1}{4}$ inch copper tubing. A
piece of tube about 20 inches long will make about the right size
worm. From the cooler, the gases are dried by passing through
6 inches of thoroughly dehydrated calcium chloride. They
then enter the weighed potash bulb and its calcium chloride
tube, which are in one piece. These bulbs are extra large at
the part holding the potash solution, being 1 inch long and
$\frac{3}{4}$ inch wide, weighing, when filled for use, about 75 grams, and
holding 30 cc. caustic potash solution. They, therefore, allow
the gases to come in contact with more of the solution for a
longer time.[1] The guard tube is the usual calcium chloride tube.

It is absolutely essential that all the calcium chloride used
should be thoroughly dehydrated, that none of the fine powder

[1] These bulbs were made to order by Queen & Co., Philadelphia.

be placed in the tubes, particularly that one attached to the
weighed potash bulb, and that as little of the space within the
tubes as is possible be taken up with cotton, which does no good
as an absorbent. It is best to sift out the fine powder
from the dehydrated calcium chloride and take that which is
about $\frac{3}{16}$ inch diameter, or the size of a dried pea.

The apparatus being ready, the combustion is proceeded with
as follows :

A stream of water is started through the water-jackets, the
burners under the spiral and copper oxide lighted, also the 3
burners of the furnace, which are regulated so the tips of the
flames just touch the curved fire-brick upon which the porcelain
tube rests. After ten minutes the burners may be turned on
sufficiently far to bring that part of the tube within the furnace to
a red heat and hold it there. The water overflowing from the
can should be about 15°C. The weighed potash bulb having been
connected, a current of air is started through the apparatus at
the rate of about 5 bubbles per second in the weighed bulb (this
is a little faster than one can count), the stopper at the forward
end of the combustion tube is withdrawn and, as quickly as pos-
sible, the platinum boat containing the carbon residue obtained
by the standard method of solution of steel, is pushed into the
tube until it meets the pipe stem, and the stopper immediately
replaced. The air is then turned off and replaced by a current
of oxygen at a slightly slower rate of speed, about $4\frac{1}{2}$ bubbles
per second. At the expiration of ten minutes the oxygen is
turned off and the air on at the former speed for ten minutes.
The connections are then broken, a new weighed potash bulb
placed in the train; a fresh boat containing the carbon is inserted
after removing the first one and a new combustion proceeded
with. The boats should be taken from the oven, which is kept
at 100° C., and at once put into the porcelain tube in order to
prevent a cold boat cracking the tube.

The copper oxide is always kept at a red heat, as is also the
combustion tube, as long as the apparatus is in use, from the
beginning of the day's work until its completion.

A combustion is thus made in twenty minutes, and one man,
with two of these pieces of apparatus side by side so arranged
that when the oxygen or air is turned from one it goes on to the

other, and six potash bulbs, can make 48 combustions per day of nine hours.

After each day's work it is necessary to wash the sand in the tube by running a stream of water through it; remove any moist calcium chloride from the tube next the cooler and replace it with fresh or, better still, put in an entirely new tube full of freshly dehydrated calcium chloride and dry the moist one to have it ready for use the day following. The worm also should be dried out about every two days by placing it over a burner and blowing air through it.

In our practice we have found that about 25 combustions can be made on each bulb before it will need refilling with calcium chloride and caustic potash solution. If more than this number be run on a bulb it will be found that the calcium chloride has. ceased to catch all the moisture carried from the potash solution. The latter has a specific gravity of 1.27 and is capable of absorbing 2.5 grams of carbon dioxide with perfect safety.

I append some of the results obtained by the above method of combustion and by combustion in a platinum tube.

Sample. No	Combustions in a platinum tube. Per cent. carbon.	Combustions in a porcelain tube by new method. Per cent. carbon.
16	0.836	0.832
17	0.850	0.860
17	....	0.864
17	....	0.864
1238 B C 389	0.563	0.566
1238 B C 389	....	0.552
1580	1.111	1.108
1099 C	1.087	1.075
1099 C	1.073	....
1078 C 291	1.162	1.168
1078 C 291	....	1.164
1060 C 283	0.326	0.323
R. J.	0.958	0.958
R. J.	0.955	0.953
R. J.	0.953	0.955
J.	1.067	1.068[1]
J.	1.070	....
B.	0.904	0.900[1]

[1] These results were obtained when exhibiting the apparatus before the Philadelphia Section of the American Chemical Society ; the carbon content of the steel was unknown to me at that time. The results obtained by combustion in a platinum tube are those of R. Job, chemist of the Philadelphia and Reading Railway Co., also of A. A. Blair.

Some duplicate results obtained by combustion in a porcelain tube by the new method are :

Sample No.	Carbon. Per cent.
1	0.839
1	0.839
5	0.838
5	0.832
8	0.776
8	0.779
9	0.850
9	0.855
11	0.843
11	0.842
14	0.848
14	0.853
713	1.012
713	1.019
B X	1.608
B X	1.614

The condenser or worm cools the gases so that when they reach the weighed potash bulb, there is no tendency to carry out moisture while running the bubbles at the speed of five per second. In fact, blanks have shown that the gases can pass through the potash bulb at a speed so great that the bubbles are scarcely to be distinguished and no loss in weight will be sustained.

	Gain or loss in weight of bulb.	Number of bubbles per second.
Blank	0.0000	5
"	0.0000	5+
"	+0.0003	steady stream

Two weighed potash bulbs placed one after the other and a combustion of a high carbon steel made with the oxygen running five bubbles per second and the air a trifle faster, gave the following :

Sample. No.		Before. Grams.	After. Grams.	Difference. Grams.
1905 B X 347	Weight of 1st bulb	17.4991	17.5920	0.0929
1905 B H 347	" of 2nd "	23.0177	23.01755	0.00015

A factor weight, 2.7272 grams, of the drillings was taken.

The porcelain tube may be replaced with a copper tube 16 inches long, $\frac{5}{8}$ inch in diameter, and $\frac{1}{16}$ inch walls, water-jacketed at each end for $1\frac{1}{2}$ inches, as these results show :

Sample.	Combustion in a porcelain tube. Per cent. carbon.	Combustion in a copper tube. Per cent. carbon.
Standard No. 1...................	0.529	0.529
" " 1............	0.529[1]	0.527
" " 2...................	0.544	0.545

The copper tube, however, burns out in about two weeks, while the porcelain tube, with proper care, will last for weeks, especially if at the heated portion, the boat be kept from direct contact with the tube by a sheet of platinum foil.[1]

The life of the copper oxide tube is about three months. When it is burned out, however, it is quickly replaced, by another, the water-jackets being easily melted from the old tube and soldered on the new.

The whole apparatus can be made in any laboratory at a very small cost.

Mr. Job, who now has this apparatus in use in the laboratory of the Philadelphia and Reading Railway Co., has obtained very good results, a few of which he kindly gave me.

	Combustion in porcelain tube.	
	Old method. Per cent. carbon.	New method. Per cent. carbon.
Standard No. 1...................	1.070	1.068
" " 3...................	0.937	0.937–0.942
" " 2...................	0.527	0.531
Blank...........................	....	0.0000
"	....	0.0000

It may be stated that in almost every instance where blanks have been made, the difference in weight of the potash bulb has been zero. This is due, I believe, to the cooler, which permits the gases to pass into the potash bulb at the same temperature, or a slightly lower one, at which it leaves it; consequently the gas is saturated with moisture to the same degree. For this reason, I believe the accuracy of the determinations even exceeds the results obtained by the old method where a dry train is used.

Many of the results that have been given, that is, those coming from this laboratory, have been made in the course of our every-day work by a man turning out a result every ten minutes from two of these pieces of apparatus, and they certainly show that,

[1] Old method combustion in platinum tube.

[2] Since the foregoing was written, Mr. Job has informed me that he has obtained excellent results by using a hard glass tube protected from the flames by a piece of iron, and supporting the boat within the tube in a sheet of platinum foil.

even at this rapid rate, the accuracy attained equals that of the more slow and painstaking method of combustion in a platinum tube.

It may be of interest to know that the copper oxide may be replaced by the electric spark as an oxidant to insure the complete change of the carbon to carbon dioxide. The action of the electric spark on a mixture of carbon monoxide and air, in the presence of moisture, is to produce carbon dioxide, ozone, and a very small amount of nitric acid; therefore, I removed the copper oxide from the system and placed in its stead a small glass tube through which two platinum wires were fused so that a spark would be produced between the points when a current from a Rhumkorff coil passed through the wires. Combustions were then made as usual, except that during the time of burning in oxygen, a continuous stream of sparks played between the platinum wires within the tube. The following table shows the results obtained :

Sample. No.	Method.	Weight of carbon dioxide. Grams.	Carbon. Per cent.
1.30 Standard	Electric spark as oxidant	0.1303	1.303
1257 B D	" " " "	0.0720	0.720
1257 B D	No oxidant	0.0614	0.614
1257 B D	CuO as oxidant—combustion in platinum tube	0.0724	0.724
1254 B D	ditto	0.0747	0.747
1254 B D	Electric spark as oxidant	0.0744	0.744
Pig iron	" " " "	0.4193	4.193
Pig iron	CuO as oxidant—combustion in platinum tube	0.2060	4.120*

Starch paper moistened with potassium iodide and placed just before the weighed absorption bulb was turned blue, showing the presence of ozone.

Owing to the platinum contacts of the induction coil becoming worn away with continued use and the consequent stoppage of the sparks, thus creating error, the hot copper oxide is preferred as an oxidant. Could, however, the trouble with the induction coil be simply remedied, the apparatus without the copper oxide would be the neatest, cleanest, and most compact to use.

Mr. John K. Faust has made most of the determinations in-

* In every case except that marked with an asterisk, where a half factor weight was taken, a whole factor weight, 2.7272 grams, was taken.

volved in perfecting this method of carbon combustions, and its success is largely due to his careful work, for which I sincerely thank him. I also wish to thank Mr. F. Cooper Pullman for his assistance in working up the electric spark as an oxidant.

LABORATORY OF THE CARPENTER STEEL CO., READING, PA.

SOIL HUMUS. SOME SOURCES OF ERROR IN ANALYTICAL METHODS.

BY A. L. EMERY.

DURING the past four years we have devoted considerable time in our laboratory to the analysis of California and Hawaiian soils for the purpose of determining the kind of fertilizer best adapted for each separate piece or tract of land. The analytical methods of Dr. E. W. Hilgard have been generally followed in our work and good results have been secured with the exception of the determination of humus and nitrogen in the humus. In order for a method to be practical for industrial work it must be rapid as well as accurate. Time is a very important factor. Many samples of soils require several days' leaching to free them of calcium salts and several days more for the extraction of the humus.

About two years ago while working with one of these slowly leaching soils it was observed that the caustic potash solution of humus was strongly ammoniacal. A slightly ammoniacal solution is, of course, unavoidable, for caustic alkalies will liberate the ammonia present in the form of ammonium salts and also readily decompose some of the weaker compounds of amid nitrogen. But where the time of leaching extended over several days more ammonia was apparently liberated, than was originally present in the form of these easily decomposed salts. Other work prevented further investigation at that time, and the subject was not taken up again until this winter when the rush of soil samples to the laboratory almost compelled experimenting with humus with a view of finding a more rapid method. During these experiments some interesting results developed.

Several samples of soil, washed free of calcium salts with dilute hydrochloric acid, were leached with a 4 per cent. solution of caustic potash. In the course of a few hours, varying with the

richness of the sample in nitrogen, a piece of red litmus suspended in the mouth of the flask containing the leached solution would turn blue in ten or fifteen minutes. The same solutions, after standing twenty-four hours, would liberate enough ammonia to turn the litmus blue in about five minutes, and after standing several days the change of color was very quick. In several cases the ammonia could even be detected with the nose. From 5 to 10 grams of soil were used for leaching.

The above being true, it follows that the determination of nitrogen in the caustic potash extract is always too low by the amount of nitrogen lost in the form of ammonia. This loss apparently depends on the nature of the soil sample, the time occupied in leaching, and the care taken to prevent the ammonia escaping from the leaching apparatus. Therefore, since the nitrogen in the caustic potash extract is too low, it follows that the nitrogen in the humus would also be too low. This loss of ammonia doubtless partly explains the great liability of duplicate results of the determination of nitrogen in humus to disagree, and more particularly accounts for the variation in results by different analysts.

By Dr. Hilgard's method[1] humus is determined by evaporating the solution, leached from calcium-free soil with dilute ammonia, drying to constant weight, igniting, and weighing. The difference in weight is regarded as humus.

During the process of evaporation the ammoniacal humus solution undergoes digestion at the temperature of the water- or steam-bath. Either during this digestion or during the leaching process (probably during both), ammonia is absorbed from the leaching solution and enters into stable combination with the humus extract. The free ammonia is easily expelled by evaporation, but the humus residue left in the platinum dish after being dried at 100°, or even 110° C., retains part of the ammonia at least that it has taken into combination from the leaching solution. This added ammonia is easily expelled with lime or magnesia, but not all the nitrogen of the residue is thus driven off even with dilute caustic potash. The following analyses will illustrate this point:

1 Wiley's "Agricultural Analysis," Vol. I, p. 324, § 311.

Total nitrogen in soil by direct determination. Gunning method.[1]	Humus.	Nitrogen in humus extracted with caustic potash.	Nitrogen in humus extracted with NH₃ evaporated and dried at 100°C.
Per cent.	Per cent.	Per cent.	Per cent.
0.159	1.860	0.67	0.97
0.097	0.775	4.39	9.39

It was at first thought that the difference in the per cent of nitrogen in the caustic potash extract and the ammonia extract represented the loss of nitrogen in the form of ammonia during the extraction with caustic potash, but it was found that a similar difference existed when the utmost care was exercised to prevent the escape of ammonia from the caustic potash solution, both during and after leaching.

These results led to the analysis of the soil residues which had been leached with caustic potash and those which had been leached with ammonia. *Approximately 50 per cent. of the total nitrogen originally present remained in the soil after leaching with caustic potash.*

Total nitrogen in soil.	Nitrogen left in soil after leaching with caustic potash.
Per cent.	Per cent.
0.159	0.097
0.132	0.066
0.097	0.038

The average of the second column of figures is very close to 50 per cent. of the first, or the total nitrogen in the soils. Present data is insufficient to determine whether this ratio is true for soils taken from all parts of the state. The above samples and others showing similar agreement are mostly from the Santa Clara valley.

After leaching with ammonia and drying the soil residue at 100°C. or distilling the residue until the distillate was neutral to litmus paper, from a little over ½ to 1½ the amount of total nitrogen originally present in the soil was found in the residue. Results seemed to vary somewhat with the time occupied in expelling the free ammonia from the soil residue by heat, the

[1] Ten grams of soil may be readily digested by this method.

distillation method giving slightly higher results than by drying at 100° C. This might have been expected since the conditions of the two processes are not exactly the same. One sample of Hawaiian soil containing 0.812 per cent. total nitrogen took up 0.430 per cent. of nitrogen from a 2 per cent. ammonia solution by digestion at the room temperature over night and retained it at 100° C. This gave a total nitrogen of 1.242 per cent.

These results seem to strongly indicate that the organic or mineral constituents of the soil left on the filter have the power to absorb ammonia from the leaching solution during the process of leaching to a far greater extent than has heretofore been supposed. It seemed highly probable that the soluble organic compounds in the extract, called humus extract, would also have this power of taking ammonia from the leaching solution. This point was demonstrated in the following manner : Five grams of soil, washed free of calcium salts, were distilled with lime and the nitrogen in the distillate determined. Then five grams of the same soil were extracted with ammonia after removing the calcium and magnesium salts according to Dr. Hilgard's method. The free ammonia was expelled from the extract by evaporating to dryness and the resulting residue distilled with lime and the nitrogen determined in the distillate. This was repeated with a number of samples and while the results seemed to vary considerably yet more nitrogen was invariably obtained from the ammonia extract distilled with lime, than from the soil distilled with lime. In the first case, that is where the soil was distilled with lime, it will be noted that the organic compounds which are insoluble in dilute caustic alkalies as well as the soluble ones were subjected to the action of lime in hot solution. Since lime will decompose some of these insoluble nitrogenous compounds it follows that more nitrogen should have been obtained in the first case than in the second had not the soluble organic compounds, leached from the soil, taken up nitrogen in the form of ammonia from the ammoniacal leaching solution. Hence, we conclude that Dr. Hilgard's method gives too high results for humus by the amount of ammonia taken up from the leaching solution and held in combination by the extracted organic matter.

Now, since nitrogen in the humus is determined by dividing the nitrogen in the caustic potash extract, which is too low, by

the humus, which is too high, the error would be multiplied and the result would be invariably too low. That this error is quite large and not to be neglected is clearly shown by the figures given above.

By a slight modification of the method the ammonia can be prevented from escaping during leaching with caustic potash. The following method seems to overcome all difficulties : The soil to be leached with caustic potash is placed in a funnel which is closed at the top with a stopper through which the leaching solution is admitted by a separatory funnel. The glass support of a Gooch crucible serves very well for the funnel holding the soil. The solution from the soil is run directly into dilute sulphuric acid, the bottle containing the same being sealed with a U-tube containing sulphuric acid. Gentle suction can be applied to this apparatus which greatly hastens the process without the least danger of losing ammonia.

It is more difficult to correct the second source of error; *i. e.*, the absorption of ammonia by the organic matter extracted from the soil. No very satisfactory results have been obtained although considerable time has been devoted to the matter.

Before leaching the soil for the extraction of the humus, it is washed with dilute hydrochloric acid until the filtrate shows no reaction for calcium. It is well known that the organic acids of soils form single and double salts with the alkali earths and with the oxides of some metals. Calcium is a stronger base than ammonia ; therefore, an acid that would liberate calcium ought also to liberate ammonia from these double insoluble salts. We had supposed that this hydrochloric acid solution contained practically only the nitrates and nitrites present in the soil which would be worth considering only in exceptional cases.

Total nitrogen in soil.	Total nitrogen leached out with hydrochloric acid.	Nitrogen leached out with hydrochloric acid which is liberated with lime.
Per cent.	Per cent.	Per cent.
0.159	0.037	0.011
0.812	0.049	0.036

The above results show that it is not safe to assume the insol-

ubility of organic matter and organic salts even in very dilute hydrochloric acid. We believe this also may be a source of no insignificant error in soil analysis.

It would be interesting to know whether the organic matter of soils of humid regions show the same tendency to absorb ammonia in such relatively large amounts as the soils that we have examined. This absorption of ammonia seems to take place at ordinary temperature as well as in hot solutions. The rate or maximum amount of absorption has not yet been determined. Hitherto we have regarded free ammonia as being occluded in the soil but it now seems highly probable that one of the functions of the organic matter of the soil is to absorb the free ammonia which comes to it in solution and that which is liberated in the soil itself. Possibly in nature occlusion precedes and directly aids absorption and combination.

Regarding the nature of humus little seems to be really known. If humus is regarded as the organic matter and mineral salts of organic acids extracted from soils by means of dilute alkalies we have to deal undoubtedly with a highly complicated mixture of chemical substances in various stages of decomposition and combination. Many organic nitrogenous substances are soluble in dilute alkalies without having undergone a process of decomposition. This is true of the organic matter of plants as well as that of animals. Sun-dried grass, weeds, or wood, according to the generally accepted idea of the term, would not be regarded as humus. Yet, 27.30 per cent. of a sample of clover meal dissolved in 25 cc. of a 5 per cent. solution of ammonia at room temperature by standing over night. The undissolved portion contained 2.94 per cent. nitrogen. Providing this residue took up no free ammonia from the solution, which is doubtful, 35.76 per cent. of the total nitrogen of the clover meal was readily soluble and probably more would have been dissolved had the leaching process been used.

This is more or less true of other organic substances which find their way into soils and form a part of them. While clover meal may be an excellent fertilizer much of it would, nevertheless, have to be regarded as humus by the present methods of analysis. In fact in many respects clover meal extract acts as

humus is supposed to act. Part of it forms insoluble salts with calcium and is precipitated with alcohol.

If a soil be boiled with an excess of calcium or barium salts and the soil afterwards extracted with ammonia the filtrate will usually have a color closely matching that of dilute ferric chloride. If the same soil is then leached with hydrochloric acid and again leached with ammonia, the resulting solution will have a much darker color which is often almost black. Yet barium or calcium salts precipitate the organic matter in the caustic potash soil extract, leaving an almost colorless supernatant liquid. The precipitation is not quantitative.

Further experiments are already under way in the laboratory and we hope to have further data of interest in regard to humus and soil analyses in connection with field experiments with fertilizers.

CHEMICAL LABORATORY OF N. OHLANDT & CO.,
April 2, 19c0.

LECTURE EXPERIMENTS. REVERSIBLE CHEMICAL REACTIONS.

BY W. LASH MILLER AND F. B. KENRICK.

L ECTURES on physical chemistry are, at present, less in need of experimental illustration than those on any other branch of the science, being delivered, for the most part, to small classes of advanced students, who have ample opportunity for experimenting in the laboratory. Some of the conceptions and discoveries which form the subject-matter of that department have, however, proved of such importance, that it is very desirable to incorporate them into the elementary course. This has hitherto been rendered difficult by the lack of suitable lecture experiments.

Among the most important of these discoveries, is that of the *incompleteness* and *reversibility* of a very large number of chemical reactions. The application of thermodynamical methods in the treatment of such cases is an achievement of the present day, and necessarily forms one of the chief subjects of study of advanced classes. The "average student," however, whose practical acquaintance with chemistry is limited to a course in

analysis, knows nothing of all this. He knows the chemical reaction as a quantitative, non-reversible, and practically instantaneous phenomenon.

It does not occur to him that the reactions he meets with in the laboratory have all been selected because of these very properties, which render them convenient for the purposes of the analyst ; generalizing from his one-sided experience, he is apt, half unconsciously, to form views on chemical affinity practically identical with those of Bergmann. Theories based on the rate of inversion of cane-sugar, and on Berthelot's experiments with alcohol and acetic acid—the experiments themselves are, unfortunately, quite unsuited to the lecture table—do not make much impression on one whose daily experience points in the other direction ; if anything, they serve only to accentuate the feeling of unreality associated with the '' other world'' of organic chemistry.

Reactions involving the addition and removal of water of crystallization, or the formation and decomposition of double salts or other '' molecular'' compounds are likewise unsatisfactory. To be convinced, the student must see a '' genuine'' chemical reaction, *i. e.*, one used in analysis or on the large scale in chemical manufacture, reversed before his eyes.

The following half dozen reactions have been selected from this point of view ; the instructions include all the details that we have found necessary in exhibiting them before a large audience.

I. AMMONIUM THIOCYANATE AND FERRIC CHLORIDE.

Approximately equivalent solutions of these substances are prepared, the first containing :

Ammonium thiocyanate.........................	7.5 grams
Water ....to make 200	cc.

and the second :

Commercial (basic) ferric chloride	6 grams
Concentrated hydrochloric acid (sp. gr. 1.175)....	25 cc.
Water ....to make 200	cc.

Five cc. of each are mixed in a large beaker, about two liters of (tap) water added, and the orange-colored mixture poured in equal quantities into four beakers.

To the	is added	The color becomes	Reaction.
first	5 cc. am. thiocyanate solution.	dark red	➡
second	5 cc. ferric chloride solution.	dark red	➡
third	50 cc. saturated am. chlor. sol.	almost colorless	⬅
While the fourth is kept for comparison.		orange	

If the reaction be represented by the equation

$$FeCl_3 + 3NH_4SCN \rightleftharpoons Fe(SCN)_3 + 3NH_4Cl$$

and the amount of ferric thiocyanate be judged from the depth of color of the solution, the reaction between equivalent quantities must be regarded as incomplete. The changes of color are interpreted by the arrows in the last column (indicating the direction of the reaction).

In order to show the effect of dilution in destroying the ferric thiocyanate (dissociation), equal quantities of the orange-colored mixture may be placed in two rectangular glass troughs of equal width, one of which is about twice as thick (from back to front) as the other. Water is then added to the solution in the larger trough until the level is the same in both, and a piece of white paper held at a little distance behind the two troughs. Seen from the front, the more dilute solution appears much less deeply colored than the other. For purposes of comparison, indigo or potassium permanganate may be used, which give the same color in the two vessels. Rectangular battery jars answer very well, as the change in color is so marked that unevenness in the glass is of no moment.

II. BISMUTH CHLORIDE AND WATER.

A " bismuth solution " is prepared as follows :

Commercial " bismuth trisnit " .... 40 grams
Hydrochloric acid (sp. gr. 1.175) .... 40 cc.

Rub together in a mortar, as the powder cakes; a trifling residue may be filtered off.

The reaction with water is represented by the equation :

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$
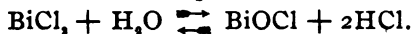
To 50 cc. water add 5 cc. bismuth solution .... ➡
Add 5 cc. hydrochloric acid (sp. gr. 1.175) .... ⬅
" 75 " water..................................... ➡
"   5 " acid .... ⬅
" 200 " water..................................... ➡
" 10 " acid .... ⬅
" 500 " water..................................... ➡
Pour in acid from the reagent bottle.................... ⬅

The reaction may be carried out in a glass cylinder, about three inches in diameter, holding about a liter. If small marks be made at the proper heights on the cylinder the water may be poured in without measuring.

Fig. 1.

The acid may be delivered from a pipette or burette, or it may be dipped out of a beaker with the little measure figured in the margin (made of a piece of test-tube and a glass rod).

III. AMMONIA WITH SALTS OF COPPER AND OF SILVER.

Silver Bromide.—Excess of potassium bromide is added to 15 cc. of fifth-normal silver nitrate solution; the precipitate is washed once by decantation, shaken with 15 cc. of ammonia (sp. gr. 0.915) and filtered. In the solution so obtained a precipitate is produced,

(*a*) adding a drop of potassium bromide solution,

(*b*) adding a drop of silver nitrate solution,

(*c*) adding five times its volume of water,

(*d*) boiling, or

(*e*) exposing (in a fractionating flask) to the vacuum of a filter-pump.

Copper Sulphate.—Five cc. copper sulphate solution (100 grams blue vitriol in 1 liter) are mixed with 5 cc. 5/1 normal ammonia and diluted with 400 cc. *distilled* water. The addition of 400 cc. more distilled water produces a precipitate. If the reaction be carried out in a flat glass cell (an inch thick) with an incandescent lamp behind it, the change from clear to turbid is very distinct. This experiment should be rehearsed immediately before the lecture, as the presence of traces of acid, carbon dioxide, or ammonia salts, largely increases the amount of water necessary to produce a precipitate. If tap water be used instead of distilled water, half as much again may be required.

IV. FORMATION AND DISSOCIATION OF WATER, ETC.

Eudiometer.—A very convenient lecture table eudiometer con-

sists of a straight glass tube (10 mm. diameter and 760 mm. long) open at one end and fused to a capillary with capillary tap at the other. The platinum wires are sealed through the wide tube just below its junction with the capillary, and the divisions are marked with rings of Brunswick black. A piece of iron pipe, widened at the mouth, serves as a mercury trough.

Measured volumes of the various gases (H_2, O_2, CO, Cl_2, etc.) may be admitted through the tap, if the eudiometer be first filled with mercury, and the division corresponding to the volume desired be set level with the surface of the mercury in the iron tube.

The union of two volumes of carbon monoxide with one of oxygen may be shown by introducing a little 30 per cent. potash above the mercury in the eudiometer; while in a subsequent experiment (without potash) the volume of the carbon dioxide formed may be determined.

The formation of hydrochloric acid from one volume of hydrogen and one of chlorine may be shown with a fair degree of accuracy, if the mercury trough

Fig. 2.

be replaced by brine from the chlorine gasometer in a tall glass cylinder.

In many cases, notably with CO and O_2, the gases must be mixed by shaking the tube vertically before passing the spark, or no explosion will occur.

Deville's Tube (Fig. 3.).—A coil of platinum wire hung vertically in the neck of a fractionating flask and heated by electricity, is just as efficient as any other "white hot platinum tube" in bringing about the dissociation of water vapor. It works very much better than the noisy induction sparks commonly employed.

If concentrated ammonia (sp. gr. 0.880) be warmed in the flask, the apparatus may be made use of to effect the decomposition of NH_3 into N_2 and H_2.

V. SULPHURIC ACID AND SODIUM CHLORIDE.

1. Concentrated sulphuric acid is poured into its own volume
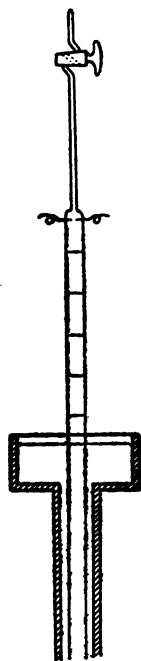
of a saturated solution of common salt in a test-tube.   The mix-
ture may be cooled under the tap and shaken ; but in general a
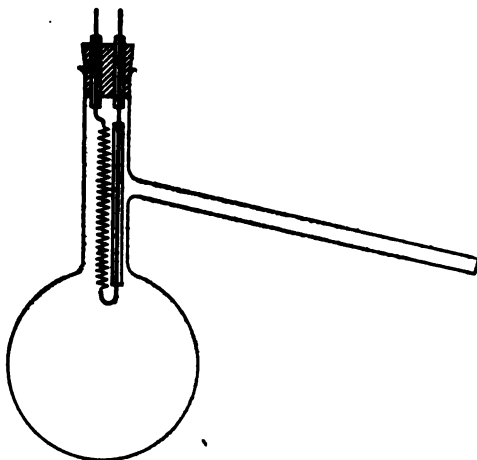
Fig.3.

crystal of Glauber's salt must be added before crystallization
will occur.   The liquid is poured off, and the crystals dried on
a piece of unglazed porcelain.

2. If some of the sodium sulphate so prepared be covered with
concentrated hydrochloric acid (on a watch-glass) it is at once
changed to a fine powder of sodium chloride ; which, in turn,
may be freed from acid on a porous plate.

To demonstrate the change from chloride to sulphate, and
back again, mix a drop of the original salt solution with a little
water on a piece of glass the size of an ordinary lantern slide ;
warm till crystallization sets in, and throw the image on the
screen (Fig. 4).   The same may be done with small portions of
the sulphate (Fig. 5) and sodium chloride formed in the ex-
periment.

VI. ANTIMONY CHLORIDE AND HYDROGEN SULPHIDE.

An antimony solution is prepared as follows: Dissolve 2 grams
tartar emetic in 15 cc. hydrochloric acid (sp. gr. 1.175) ; then

add 85 cc. water. (This solution cannot be kept more than two **or three** hours as a precipitate of oxychloride is slowly formed.)

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl.$$

(*a*) Pass a little H_2S into 5 cc. antimony solution........ ▬→
(*b*) Add 8 cc. hydrochloric acid (sp. gr. 1.175) .... ←▬
(*c*) " 5 " antimony solution......................... ▬→
(*d*) Heat, not to boiling................................ ←▬
(*e*) Cool again (in a dish of water) .... ▬→
(*f*) Add 6 cc. hydrochloric acid......................... ←▬
(*g*) Pass in H_2S under pressure of 3 meters Hg.......... ▬→
(*h*) Reduce pressure by filter-pump .... ←▬

Notes.—(*c*) If the addition of antimony does not bring down
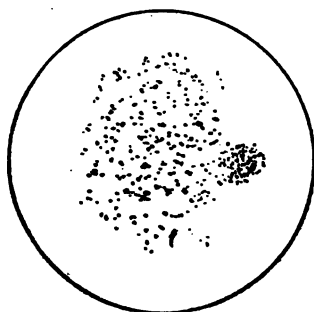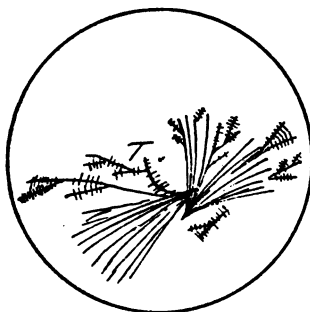
Fig. 4.   Fig. 5.

a fairly heavy precipitate, hydrogen sulphide should be passed in again, or there will be no precipitate in (*e*).

(*e*) Cool only until a precipitate appears, then add the acid (*f*) and finish|cooling ; if too much precipitate is formed it dissolves very slowly in the acid.

(*g*) The necessary pressure may be secured by means of the pump described below. With a rubber "syringe" (bulb and two valves) worked by hand, a pressure of about one meter of mercury (above the atmosphere) may be maintained; this is sufficient for the purposes of the experiment, but the precipitate comes much more slowly than when the pump is used. The object of the vacuum (*h*) also is to save time.

The reaction may be conveniently carried out in the glass ves-

sel represented in Fig. 6.   The hydrogen sulphide enters by *A* which may be tied in by wire round the ears *E*.   *A* is connected to the pump by rubber pressure tubing, and *B* (the outlet) to
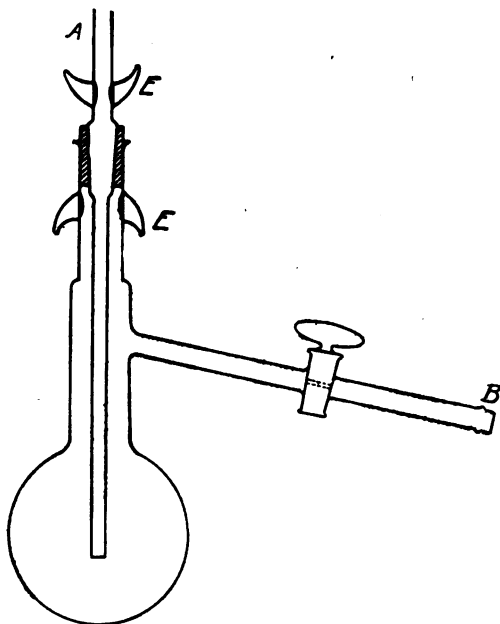
Fig.6.

the flue.   All taps should be wired in.   Joints may be made with ordinary rubber tubing covered with cloth and wired.

VII. PRESSURE PUMP FOR GASES.

The accompanying figure (Fig. 7[1]) represents the pump referred to in the preceding paragraphs.   It consists of three pieces of black rubber tubing T (of which two are shown in the figure) each 1 inch in diameter and 18 inches long, closed at the bottom and connected at the top by glass tubing to a pair of Bunsen valves.   The valves are shown separately in Fig. 8 and are so arranged that on compressing the tubes the gas contained in

[1] For the sake of clearness, the taps and handle which are actually *behind* the cylinder, are represented *to one side* of it.

them is forced out through D, and on removing the pressure
they are refilled through F.

The compression is effected by moving the handle H to the
position indicated in the figure, thereby opening the brass tap
W (communicating with the water mains) and closing S (to the
sink). Water thereupon flows through the glass pipe P into the

Fig. P.
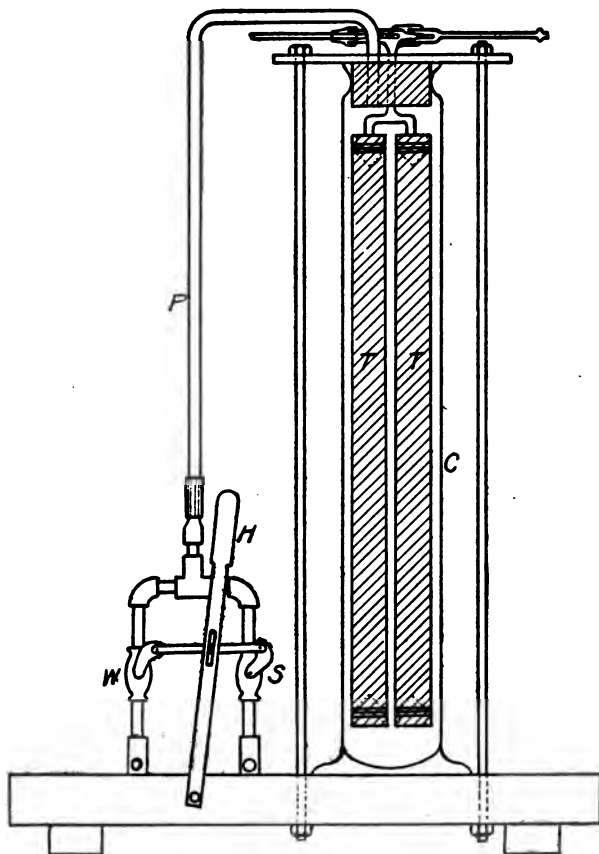
glass cylinder C containing the rubber tubes T. Moving the
handle in the opposite direction fills the tubes again with gas.

The top of the cylinder is closed by a rubber plug covered with
a brass plate ($\frac{1}{4}$ inch thick) which is held down by four $\frac{1}{4}$-inch

brass rods threaded at the ends and provided with nuts. The ends of the tubes are closed by glass plugs, wired in ; in order to keep the rubber from tearing, a wedge-shaped piece of cork is inserted at each end, as shown by the dotted lines in the figure.

The capacity of the pump is 500 cc. Three strokes are suffi-
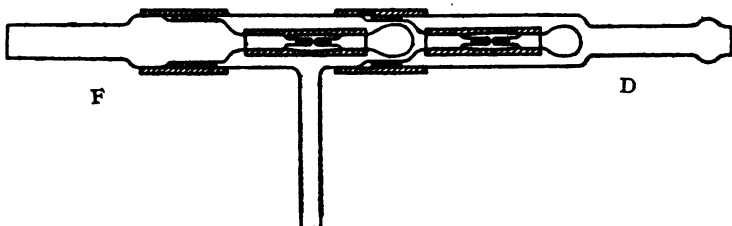
Fig. 8.

cient to attain the maximum pressure in the antimony sulphide experiment.

With this apparatus a gas can be brought to the pressure of the water system *without coming into contact with any liquid*. Higher pressure may be attained by using a force pump ; the limit depends only on the strength of the apparatus and on the ratio between the variable volume (rubber tubing) and the constant volume (glass tubing) between the valves.

THE CHEMICAL LABORATORY OF THE UNIVERSITY
OF TORONTO, April, 1900.

A NEW ELECTROLYTIC CELL FOR RECTIFYING ALTERNATING CURRENTS.

BY W. L. HILDBURGH.

IN electrical work an automatic device which will permit a current to pass through it in one direction only is frequently . desirable, for rectifying alternating currents, for example, or for preventing a back-flow of current due to polarization. In addition to mechanical commutators several arrangements for the purpose have been previously known. but, with one exception, they are applicable to comparatively high voltages only. This exception is the two-cell rectifier described by Prof. M. I. Pupin

before the American Physical Society.[1] In the present paper a new class of electrolytic cells capable of affecting currents of extremely low voltage is described. These cells act by the production of a counter E. M. F. of polarization whose intensity depends on the direction of the E. M. F. impressed, and have been termed "Single Cell Rectifiers."

If a plate of copper be placed in dilute sulphuric acid it will not dissolve. If, however, a platinum electrode be placed in the acid, and the copper made the anode, a very small E. M. F. is sufficient to cause the copper to dissolve freely and hydrogen to be deposited on the platinum, and a current will pass until all the copper is carried into solution. When the source of the E. M. F. is reversed a momentary current passes, the platinum plate becomes covered with oxygen, and, if the impressed voltage is not too high, the current ceases almost completely. That is, the cell Cu | H$_2$SO$_4$ | Pt, producing no current, permits the passage of continuous currents of low E. M. F. through it in one direction only.

By placing a number of such cells in series it is possible to prevent the flow of a current of any voltage whatsoever. Such a cell may be used for the rectification of alternating currents by so regulating the size of the platinum plate that the quantity of current necessary to polarize it as anode is less than that which passes during the next half-wave, when the platinum acts as cathode. The smaller the platinum, or passive plate, the higher the degree of rectification (asymmetrical efficiency) attainable. The amount of rectification is dependent, however, not only on the size of the passive plate, but also on the quantity of current which can pass; that is, on the *current density* at the surface of that plate. Consequently the lower the resistance in the circuit or the lower the frequency of the alternating E. M. F. impressed the greater will be the asymmetrical efficiency.

In the cell Cu | H$_2$SO$_4$ | Pt, or more properly speaking, Cu | CuSO$_4$ | H$_2$SO$_4$ | Pt, considerably more energy is required to produce hydrogen at the passive plate than is given out by the solution of the copper, or active plate. As this evidently lowers the efficiency of the device by producing an E. M. F.

[1] June, 1899.

counter to the main flow of current, means should be adopted of making the energy given out at the active plate and that absorbed at the passive as nearly equal as possible. By making the active plate of the substance given off at the passive plate by the current in the "useful" direction this condition can be nearly fulfilled. The substance produced at the passive plate should be a gas, as otherwise that electrode will soon become covered with a layer of active substance and cease to be inert. Gaseous active electrodes may be formed with hydrogen, oxygen, chlorine, etc., as the active material, absorbed by platinum or in chemical combination with some metal.

Of such electrodes the writer has found that hydrogen when absorbed by platinum black gives by far the best results, and can be made, in addition, self-regenerating, giving a "continuous-acting" rectifier such as is shown in illustration. V is a sealed vessel into which pass two mercury-contact electrodes A and P. A, the active plate, is of platinized platinum, partly in hydrogen
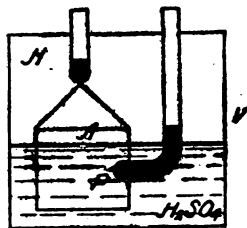
gas (H) and partly in sulphuric acid (H_2SO_4). P, the passive electrode, is a platinum wire sealed into glass and cut off to give the desired surface of contact with the liquid, or filed plane with the sealed end of the tube. The "useless" current carries oxygen to P, but is of insufficient voltage to produce bubbles, and the cell polarizes. In the opposite, or "useful" direction hydrogen is carried from A to P, is there given off in bubbles, and goes back to join again the gas H. It is clear that since nothing but hydrogen is produced at P, provided the impressed E. M. F. is not too high, that the cell will work for an indefinite time, or until changes in the surface of the platinum electrodes stop the actions described.

For the most perfect action of rectifiers of this class there

should be no counter E. M. F. in the "useful" direction. In the hydrogen-cell it requires from a few thousandths of a volt to 0.085 volt to carry the gas through the electrolyte, the pressure varying with the size of the passive electrode and the condition of its surface, the concentration of the liquid, the temperature, etc. This counter E. M. F. can be "balanced," as is necessary for certain kinds of work, by adding an E. M. F. in the "useful" direction, taken from a slide-wire in series with 1 or 2 cells of battery.

It is impossible to specify the size of the various parts of a cell without knowing all the conditions under which it is to be used. As a general rule the small (passive) electrode should be of the dimensions of a millimeter, ranging in area from a small fraction of 1 sq. mm. up to 100 sq. mm., according to the frequency and the resistance or inductance in the external circuit. The platinized electrode should be of sufficient size to absorb hydrogen as fast as it is given off at the passive plate. For the electrolyte 1 part sulphuric acid to about 8 or 10 of distilled water, from which the oxygen has been removed by boiling or exhaustion, serves very well. The vessel need only be large enough to contain the two electrodes and a little liquid and gas, the latter two being employed continuously, and only a very small quantity being in use at any one time. The larger electrode should be thoroughly washed after platinizing, as otherwise platinum may be carried to the smaller electrode, impairing the efficiency. A jar of water, in which the cell may be kept, offers a convenient method of sealing, for laboratory use.

The following points will be found of service in working with the cell, and have been obtained, for the most part, by the study of curves taken with alternating currents. More complete expositions of the theory and actions of rectifiers of this class will be found in other papers by the writer.[1]

The smaller the plates the greater the asymmetrical efficiency

The greater the resistance in the circuit the less the asymmetrical efficiency.

The higher the frequency the less the asymmetrical efficiency.

The higher the frequency, or the greater the resistance, or the larger the plates, the higher may be the impressed alternating

1 *Elec. World and Eng.*, 1900; *School of Mines Quarterly*, July and Oct., 1900.

E. M. F. in a given cell, without producing oxygen bubbles at the smaller plates.

In a perfectly "balanced" rectifier, as long as the impressed E. M. F. is not too high, the quantity of current capable of doing unidirectional work is proportional to the impressed E. M. F.

If the active E. M. F. of a rectifier be too high a continuous current will flow, and the amount of rectification be dependent on the impressed E. M. F.; if the latter below, rectification may cease completely.

If the active E. M. F. be too low the amount of rectification is dependent on the impressed E. M. F., and may become zero if the latter be low. This property prevents the use of rectifiers in circuits in which any considerable counter E. M. F. is produced.

Rectifiers for high E. M. F. can be formed by joining a number of cells in series. The passive plates in each can then be correspondingly increased in size, while the whole set gives the same efficiency as one of the cells gave before its electrode was enlarged. The number of rectifiers and the impressed E. M. F. should be proportioned to their circuit exactly as primary cells are proportioned, each primary cell being represented by a rectifier and a certain portion of the impressed E. M. F.

A METHOD FOR THE DETERMINATION OF ELECTRICAL CONDUCTIVITY WITH DIRECT CURRENT INSTRUMENTS.

BY J. LIVINGSTON R. MORGAN AND W. L. HILDBURGH.

IN the determination of electrical conductivity, in order to prevent errors, it is necessary to use an alternating current whose frequency is of such a value that the electrodes, during a half period of the alternating current, receive a polarization which is negligible compared to the voltage impressed. Up to the present time it has been difficult to detect small quantities of an alternating current, except by aid of the telephone. In the

Kohlrausch-Ostwald method the electrolyte is placed in one arm of a Wheatstone bridge, an alternating current passed through it and the resistance balanced on the bridge wire against a known value by aid of the telephone. McIlhiney[1] passes a direct current through a direct current measuring instrument and then transforms it into an alternating current with a rotating pole changer and carries it through the electrolyte.

One of us[2] has designed a number of rectifying cells for the purpose of permitting the passage of current in one direction only, so that an alternating current in going through them is more or less rectified and has many of the properties of a direct one. Of these cells the most suitable for laboratory use is the continuous acting hydrogen cell, which has been applied to conductivity measurements in the following way : The apparatus for the substitution method is arranged as in Fig. 1. The alter-

Fig. 1.

Fig. 2.
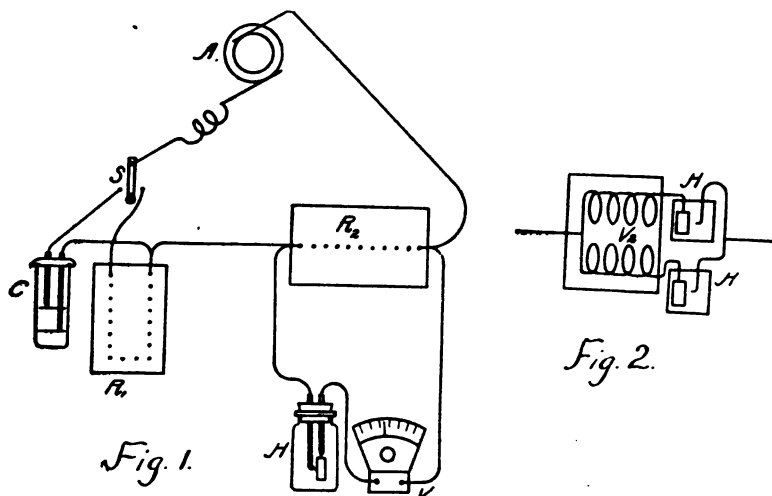
A is the source of the alternating current, S a switch allowing either C or R_1 to be in the circuit, C is the unknown resistance, R_1 and R_2 resistance boxes, H the hydrogen cell rectifier, and V the voltmeter or galvanometer.

nating c irrent from A passes through the electrolyte in C and the non-1 ·ductive resistance R_1, to the terminals of which is connected a direct current instrument in series with the rectifying

[1] This Journal, **20**, 206 (1898).

[2] W. L. Hildburgh : This Journal. Also Ph.D. thesis in press and *School of Mines Quarterly*, July and October, 1900. Also *Elec. World and Eng.*, 1900.

cell.   The reading of the instrument is noted when the current passes through the unknown resistance C, then S is moved so as to replace C by R_1, a non-inductive adjustable resistance, and this varied until the same reading is observed as before.   If the proper precautions have been observed, the resistance of R_1 is equal to C and the conductivity may be calculated.

For the source of the alternating current we have found a small alternator to be more satisfactory than the small induction coils commonly used ; there is, however, apparently no reason why a properly arranged coil should not be available.   With the ordinary (Kohlrausch) electrodes and an alternating pressure of 2 volts the results were found to agree very satisfactorily with those obtained by the Kohlrausch-Ostwald method.

For the highest sensitiveness the following conditions should obtain.   The resistance of R_1 which must be small compared with C, should be as large as possible.

The instrument V (galvanometer) should give large readings with small currents, and its resistance should be low.   The frequency of the alternating current should be as low as allowable, the voltage as high as allowable, and the electrodes in C large. The area of the inert electrode in the rectifier should be small so as to give a high asymmetrical efficiency (percentage of rectification).

A considerably more sensitive arrangement is obtained by replacing R_1, H and V by a differential wound instrument whose two windings are exactly alike and are in series each with a rectifier.   If these two coils are properly arranged all waves of one sign will go through one winding, and all of those of the opposite sign through the other (Fig. 2).   This utilizes the whole of both half waves of current, instead of only a part of one, so that the deflection of the needle is very much greater.

The hydrogen cell rectifier can be "balanced" by adding a small electromotive force in series, so that up to a certain point a direct current instrument in series with it will give readings almost exactly proportional to the alternating current.   Knowing the alternating voltage, the rectification constant of the hydrogen cell and the resistances of C and H, the resistance of C can be calculated directly from the readings of V.   This method can be used without "balancing" the cell by calibrating V, using

different known resistances in place of C. The resistance of C can then be read directly from the scale of the instrument. In both these modifications the frequency of the alternating current must remain the same, and neither is as accurate as the first one by substitution.

The hydrogen cell rectifier permits the use of an optical detector instead of the telephone in the Kohlrausch-Ostwald method. The telephone is replaced by a resistance and a sensitive galvanometer in series with the "balanced" cell, arranged like R,V and H in Fig. 2. The point on the slide wire which gives no deflection is then the same one as found by the telephone.

To "balance" the cell the circuit of a Leclanché is closed through a high resistance and a slide wire. The alternating current being stopped, an electromotive force is taken from the slide wire and sent through the rectifier, the slide being left just below the point which shows deflection. If "overbalanced" the cell will give a constant deflection, but if "underbalanced" the low voltage current obtained will give no deflection. An arrangement like Fig. 2 will give here greater sensitiveness, but the method of substitution as first described is the simplest and gives the best results.

ON THE PREPARATION OF POTASSIUM XANTHATE FOR NICKEL DETERMINATIONS.

BY E. D. CAMPBELL.

IN 1895 the author with W. H. Andrews published a method for the determination of nickel in nickel steel.[1] This method has been in use in this laboratory since its publication and has given very satisfactory results, provided the potassium xanthate used had been properly prepared. The potassium xanthate usually found on the market has not been satisfactory owing to the fact that the salt after making has not been carefully washed and dried. The practice in this laboratory has been to have each student prepare the potassium xanthate used in his own work.

1 This Journal, 17, 125.

The method of preparation is as follows: A weighed amount of fused potassium hydroxide is placed with absolute alcohol in a tightly stoppered flask and digested cold, with occasional shaking, until solution is complete, except for the small amount of potassium carbonate usually present; 2.5 cc. of absolute alcohol should be used for each gram of potassium hydroxide.

The clear solution of potassium hydroxide is poured off from any undissolved carbonate into a beaker and cooled by standing in ice-water. Pure carbon disulphide is now gradually added with constant stirring until 1 cc. has been added for each gram of potassium hydroxide used. When all the carbon disulphide has been added the stirring is continued, the beaker being kept in ice-water until the temperature is reduced to 10° C. or below.

The formation of potassium xanthate takes place according to the reaction:

$$KOH + C_2H_5OH + CS_2 = KC_2H_5COS_2 + H_2O.$$
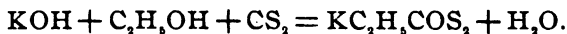
The precipitated salt is transferred best to a Buchner funnel in which a filter-paper has been laid, and the solution drawn out by means of a pump. When the solution has been drawn through, the precipitate is pressed rather firmly down in the funnel and washed once by pouring over it just enough absolute alcohol to cover it well. When the alcohol has been drawn through, the precipitate is washed twice in a similar manner with ether. The washed xanthate thus prepared is thoroughly dried at about 100° C. and after pulverizing is ready for use.

We have found that potassium xanthate made by the above method is perfectly stable, just as accurate results having been obtained with xanthate that had been kept three years as with the fresh material. With ordinary care in preparation, the yield of potassium xanthate is about 10 per cent. greater than the amount of potassium hydroxide used.

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ON THE RELATION OF THE REDUCING POWER OF NORMAL URINE TO THE AMOUNT OF CERTAIN NITROGEN COMPOUNDS PRESENT.

BY J. H. LONG.

THE reducing power of normal urine is easily observed by the application of certain reagents and was at one time supposed to be largely or mainly due to the presence of dextrose or some similar body. In fact, based on the reducing power alone, estimates of the amount of carbohydrates in urine were frequently made and are still occasionally found in the text-books of urine analysis and physiological chemistry. Later, doubt was thrown on this conclusion and the presence of even traces of sugar in normal urine was disputed. Seegen[1] made many experiments in this direction and came to the conclusion that if any sugar at all is present it cannot be in amount above 0.006 per cent. The same result essentially was reached by several others, but in most cases the methods of examination employed were open to criticism as they did not provide for the actual separation and identification of a sugar, supposing it present.

Meanwhile E. Fischer[2] proposed the reaction for the separation of sugars by the phenylhydrazine test, and von Jaksch[3] and

[1] Ztschr. physiol. Chem., 9, 332.
[2] Ber. d. chem. Ges., 17, 579 and 20, 82.
[3] Ztschr. anal. Chem., 24, 478.

others applied it to the identification of sugar in urine. Baumann[1] showed the ready production of benzoic esters of dextrose and this general method was soon applied in urine examination by Wedenski,[2] Roos,[3] Salkowski,[4] and others. The amount of the pentabenzoic ester found in this way was quite variable but always small. In Salkowski's test the range was from 1.22 grams to 3.36 grams in 1000 cc. of urine representing the whole day's excretion. In Wedenski's experiments the maximum amount was ten times the minimum found. Later Baisch made two important contributions on the subject of the nature and amount of the carbohydrates in the urine[5] and places the content of these bodies somewhat higher than Seegen, but still very low. His results give the average excretion of reducing carbohydrates as 0.100 gram to the liter. About the same time Allen published an interesting paper on the subject[6] and reached nearly the same result.

It is quite evident from the foregoing that while the existence of sugar in the urine may be looked upon as settled, the amount is very small and far from accounting for the total reduction. This has been reported by some authors as corresponding to 0.15 per cent. of dextrose while others place it as high as 0.4 per cent., in the mean.

NATURE OF THE REDUCING BODIES.

When speaking of reduction the behavior toward some metallic solution, generally toward copper oxide, is usually in mind. Among substances, other than sugar, which occur normally in urine the most important from the standpoint of this behavior are doubtless uric acid and creatinin. Glycuronic acid is often referred to as having an important action here, but the amount ordinarily present is too small to be practically considered in comparison with the others. The reducing power of uric acid has been long known and under certain definite conditions an equation may be written expressing the amount of oxygen absorbed in passing into several related bodies. The reducing

[1] *Ber. d. chem. Ges.*, **19**, 3218.
[2] *Ztschr. physiol. Chem.*, **13**, 122.
[3] *Ibid.*, **15**, 513.
[4] *Ibid.*, **17**, 229.
[5] *Ibid.*, **18**, 193 and **19**, 339.
[6] *Analyst*, **19**, 178.

power of creatinin is fully as important as is that of uric acid, and besides it is more readily followed and measured.

It occurred to me, therefore, that some light could be thrown on the question of what part a sugar plays in the total reduction by determining as accurately as possible in a large number of normal urines the amount of uric acid and creatinin present, and calculating then the reducing power of these from their relations to the oxidizing solution previously determined. The difference between the total reduction and that due to these bodies would roughly measure the reducing power of the sugar present, provided no other substance has been overlooked which exhibits the same action. The possibility of the existence of such a substance or substances in the urine must, of course, be conceded, especially since the ratio of carbon to nitrogen present, as found by direct analysis, is much higher than that calculated from the sum of the determinable constituents present. The new substance recently separated from urine and called oxyproteic acid by Bondzynski and Gottlieb[1] is supposed by Pregl[2] to account for this ratio, and to be, after urea, the most important body in the urine. The analyses made by Pregl show it to contain about 30 per cent. of carbon and 8 per cent. of nitrogen, and to amount to 6 or 8 grams daily. He states, however, that the product, as separated by his methods of precipitation and purification, is quite devoid of any reducing action on alkaline copper solutions. Toepfer has also recognized this peculiar urinary acid[3] but claims that the amount found by Bondzynski and Gottlieb is too high, because the barium salt separated is always impure from presence of much coprecipitated matter. It is certainly remarkable that an acid as abundant as this is supposed to be, should have so long escaped detection, and this fact suggests caution in generalizing too much from the results of urine analyses, however carefully they may be made; but up to the present time no substances have been found in the urine in sufficient quantity to account for the reducing power save those mentioned, and it is from this, as a working basis, that the following investigation was undertaken.

While many substances have been employed as reagents in

[1] *Centralblatt für Physiologie*, 11, 648.

[2] Pflüger's *Arch.*, 75, 87, 1899.

[3] *Centralblatt für Physiologie*, 11, 850.

this reduction test some form of copper solution has usually been found practically the most useful. A weak solution of methylene blue is reduced readily by sugar and creatinin in alkaline solution, and very slowly by uric acid, but as the reduced product is oxidized with extreme readiness in contact with air, with return of the blue color, the reagent is not suitable for quantitative measurements. A weak solution of safranine is also reduced by sugar in alkaline medium and apparently not at all by uric acid or creatinin, but the amount of sugar necessary to produce an appreciable effect is greater than that usually found in normal urine, so that this reagent is not practically available. Measurement of reduction by aid of bismuth or mercury salts is also possible, but, as is well known, the methods are lacking in delicacy.

Among the various copper solutions used in sugar analysis there are several which may be employed with very weak solutions corresponding to normal urine. The best of these appears to be some form of the ammonia-copper solution recommended by Dr. Pavy. This was first made by diluting 120 cc. of Fehling's solution with 300 cc. of strong ammonia and water enough to make 1 liter. Pavy assumed that each cubic centimeter of this solution oxidizes 0.5 mg. of dextrose, and has, therefore, one-tenth the strength of the ordinary Fehling solution, which is approximately true. Several modifications of the solution have been proposed with variations in the amounts of copper sulphate, ammonia, and fixed alkali. Finally, the Loewe solution containing glycerol has been made the basis of the dilution, instead of the Fehling solution containing a tartrate ; the Purdy solution is made in this way.

As the oxidizing power of the solution changes with these variations, it is important to recognize the extent of this alteration and allow for it if necessary. The composition of several of the best known of the modifications is here given, the original Pavy solution being added for comparison. The volume is one liter in each case.

	Copper sulphate. Grams.	Sodium hydroxide. Grams.	Rochelle salt. Grams.	Glyc-erol. cc.	Ammonia. 0.90. cc.
Pavy	4.158	(7.20)	20.76	..	370
Hehner	4.502	15.6—19.5	22.49	..	370
Purdy	4.752	23.5 KOH(= 16.8 NaOH)	....	38	350
Peska	6.927	10.00	34.50	..	135

Variations in the oxidizing power of each solution follow mainly from alterations in the amount of fixed alkali or ammonia used, and this is shown in some tests to be now given. I made solutions as follows :

A.

Copper sulphate, cryst············· 5 grams.
Caustic soda (100 per cent.) ············· 18 "
Glycerol············· 35 cc.
Water, to make············· 250 "

B.

Ammonia water ············· 0.90 sp. gr.

These solutions were mixed in the proportions given below and used in the titration of a 0.2 per cent. dextrose solution in the usual manner. The results are shown in the following table:

TABLE I.—REDUCTION WITH AMMONIA VARIABLE.

Vol. of Sol. A. cc.	Vol. of Sol. B. cc.	Vol. of water. cc.	Sugar solution required. cc.	Mg. of $CuSO_4.5H_2O$ to 1 mg of $C_6H_{12}O_6$.	Mols. of CuO to 1 mol. $C_6H_{12}O_6$.
25	75	∞	28.5	8.772	.6.32
25	60	15	29.5	8.474	6.11
25	50	25	30.3	8.251	5.95
25	40	35	30.8	8.117	5.85
25	30	45	31.4	7.962	5.74

The oxidizing power varies greatly with the amount of ammonia present and is decreased with increase in the latter. The change amounts to about 10 per cent. of the whole in the limits given.

The effect of adding an excess of sodium or potassium hydroxide is even more marked as was found by experiments given below. The following solutions were made :

C.

Copper sulphate, cryst ············· 5 grams.
Glycerol ············· 35 cc.
Water, to make ············· 250 "

D.

Strong ammonia water ············· 0.90 sp. gr.

E.

Sodium hydroxide, 100 per cent ············· 50 grams.
Water, to make············· ············· 250 cc.

These solutions were mixed in different proportions and were used to test a dextrose solution of about 0.2 per cent. strength. The results obtained were as follows :

TABLE II.—REDUCTION WITH FIXED ALKALI VARIABLE.

Vol. of Sol. C. cc.	Vol. of Sol. D. cc.	Vol. of Sol. E. cc.	Vol. of water. cc.	NaOH in grams per liter. Grams.	Sugar solution required. cc.	Mols. of CuO to 1 mol. $C_6H_{12}O_6$.
25	35	25	15	50	34.8	5.18
25	35	20	20	40	33.3	5.41
25	35	15	25	30	32.0	5.63
25	35	10	30	20	30.4	5.93
25	35	5	35	10	28.7	6.28
25	35	2.5	37.5	5	28.0	6.44

We have here an extreme variation of about 25 per cent. in the oxidizing value of the copper solution. As the fixed alkali itself possesses marked oxidizing power, as shown, in fact, in our ordinary Moore's test for sugar in urine, the increase in alkali must add to the oxidizing power of the finished solution. Hehner has shown that the solution can be made and will oxidize perfectly without the addition of any fixed alkali, but the action is then very slow and the oxidation ratio still lower.[1]

These experiments indicate that to secure anything like uniformity in the results obtained by the Pavy solution or its modifications, care must be taken to employ definite and constant amounts of fixed alkali and ammonia. The statement of Allen ("Chemistry of Urine," p. 67, 1895) that considerable variation in the amount of caustic alkali and ammonia may be made in the Pavy solution without altering appreciably its oxidizing value, does not appear to be correct. Of the two cheap fixed alkali hydroxides, caustic soda is preferable to caustic potash and is much more commonly used.

Variations in the amount of glycerol or tartrate are of less importance, but still have an appreciable influence, as I have found in several trials. As the great excess of ammonia present is sufficient to hold the copper hydroxide in solution, it is not necessary to use a large amount of either.

In the Pavy and Purdy liquids the oxidizing power is apparently assumed to be independent of the strength of the sugar solution added. Pavy and Purdy assume the factor 8.316 grams of

[1] Analyst, 6, 219.

$CuSO_4.5H_2O$ to 1 gram of $C_6H_{12}O_6$. But Peska has shown that the factor varies over 2 per cent. with solutions ranging from 0.1 to 1 per cent. in strength.[1]

As in practical work it is desirable to employ a solution, 1 cc. of which oxidizes some simple unit amount of sugar. I have used one in the work below with a value of 1 cc. for each milligram of sugar oxidized in 0.2 per cent. solutions. It is made with the following amounts per liter :

Copper sulphate, cryst	8.166 grams.
Sodium hydroxide (100 per cent.)..........	15.000 "
Glycerol	25.000 cc.
Ammonia water (sp. gr. 0.9)	350.000 "
Water, to make............................	1,000.000 "

The value of this solution in copper oxide, CuO, is 2.6042 grams per liter, and 1 molecule of sugar $=$ 5.88 molecules of CuO, as it is employed.

Of the solution, I use 50 cc. and dilute with water to 100 cc. To prevent too rapid an escape of ammonia and avoid reoxidation to some extent, I add to the mixture, while warming, enough pure white solid paraffin to make a layer of 3 or 4 mm. in thickness when melted. The burette tip for discharging the sugar solution or urine is made long enough to pass down the neck of the flask and below this paraffin. By boiling gently and adding the weak saccharine liquid slowly, very close and constant results may be obtained. At the end of the titration the paraffin is solidified by inclining the flask and immersing it in cold water, or by flowing cold water over it. The reduced liquid is then poured out and the cake of paraffin is thoroughly washed for the next test. A flask so prepared may be used for a hundred titrations. The solid paraffin is much preferable to the oil recommended by Allen and Peska. To prevent bumping and facilitate easy and uniform boiling, I add a few very small fragments of pumice-stone.

A solution made as above is not too strong in copper for accurate work, but the volume of ammonia necessary to hold a much larger amount of the reduced oxide in solution would render the process very inconvenient. The sugar employed in fixing the value of the above standard solutions was a very fine sample of

[1] *Ztschr. anal. Chem.*, **35**, 94.

pure crystal dextrose made for me by Dr. Gudemann, of the Chicago Sugar Refining Co.   It was further purified by crystallizing from hot alcohol.   After careful drying at 80° C., it was examined by a very accurate polarimeter and found to have a degree of purity not less than 99.9 per cent.

An ammoniacal solution made in this way and used with the layer of paraffin is preferable to the usual Fehling liquid in the titration of weak dextrose solutions.   It cannot be conveniently used for strong solutions, however, because of the large volume of standard required to oxidize a small volume of the saccharine liquid.

The behavior of this solution with the weak sugar solutions being established, it remains to show how it acts with creatinin and uric acid.

CREATININ AND COPPER SOLUTIONS.

The importance of creatinin as a reducing body is commonly overlooked although referred to in Neubauer ·and Vogel's "Urine Analysis," and in other large works.   This is partly due to the fact that the amount present is generally underestimated, as shown by the figures given in several of our best known handbooks of urine analysis.[1]   The reducing effect of creatinin on alkaline copper solutions has been observed by Worm Müller,[2] Johnson,[3] and others.   Müller places the reducing power low, 1 molecule of creatinin to not over 0.75 molecule of copper oxide.

Johnson states that 4 molecules of ordinary creatinin have the same reducing action on copper salts as 2 molecules of grape-sugar, and that this reduction plus that due to the uric acid will account for the whole of the reducing action found in normal urine.   The presence of sugar is disputed.   The results of Müller and Johnson, are widely divergent, which is doubtless due to essential differences in the methods of observation.   The reducing power of creatinin is shown only after long warming in the ordinary Fehling titration, and at the outset the cuprous oxide formed is held in solution, which is a disturbing element in making the test.   But with the weak ammoniacal solution

[1] See on this point, Allen, *loc. cit.*
[2] *Ztschr. anal. Chem.*, **21**, 610.
[3] *Chem. News*, **55**, 304.

used for the sugar the behavior is quite different. The reduction appears to proceed as regularly and normally as with sugar itself. I have made a number of tests with solutions of different strengths, but all weak, and find that about 92 mg. of creatinin are required for 50 cc. of the standard copper solution containing 2.604 grams of CuO to the liter. This corresponds almost exactly to the proportion, 1 molecule $C_4H_7N_3O$: 2 molecules CuO, which is about one-third the reducing power of dextrose under the same conditions. The result is much larger than that of Worm Müller, but lower than the figures given by Johnson. The actual reducing values are given in the table below. The creatinin used was prepared in the laboratory and was practically pure.

TABLE III.—REDUCING POWER OF CREATININ.

Creatinin in 100 cc. Mg.	Copper solution taken and diluted to 100 cc. cc.	CuO equivalent. Mg.	Creatinin solution used. cc.	Creatinin to 130.2 mg CuO. Mg.	Mols. CuO to 1 mol. $C_4H_7N_3O$.
50	25	65.1	92.5	92.5	1.998
50	25	65.1	94.0	94.0	1.967
120	50	130.2	76.0	91.2	2.026
120	50	130.2	77.0	92.4	2.000

Mean, 1.998

The oxidation of creatinin by alkaline copper solutions is usually explained on the assumption that oxalic acid and methyl guanidin are formed, the creatinin being first converted into creatin by the alkaline solution,

$$HN=C=NH_2.NCH_3.CH_2CO_2H + O_2 =$$
$$C_2H_2O_4 + HN=C=NH_2.NHCH_3.$$
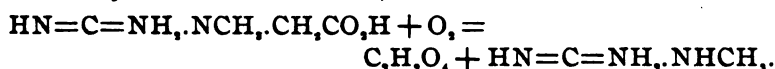
In the above experiments, however, the amount of oxygen absorbed corresponds with only half that necessary for this equation, and under the condition none can come from the air. The reaction must therefore take place in a different manner, which appears all the more probable in view of recent work by E. Wörner,[1] and Toppelius and Pommerehne,[2] who found that the reduction is variable with time of boiling with strong Fehling solution. With weak solutions the reduction is slow, but on boiling 5 cc. of a weak creatinin solution an hour with 60 cc. of strong Feh-

[1] *Ztschr. physiol. Chem.*, 27, 1.
[2] *Archiv. der Pharmacie*, 234, 380.

ling solution a much greater effect is observed. Under such conditions 1 molecule of creatinin appears to reduce over 4 molecules of CuO. It is quite possible that the oxidation of creatinin is preceded in weak solution by hydrolysis with formation of ammonia and methyl hydantoin and that this body is afterwards oxidized in several stages. The reduction of 4 molecules of CuO would correspond to the oxidation of the acetic acid group in creatin to oxalic acid, as required by the equation written above, but in the ordinary application of the copper tests in urine analysis no such degree of oxidation is likely.

URIC ACID AND COPPER SOLUTIONS.

The behavior of uric acid with alkaline copper solutions has been described by several chemists and notably by Riegler[1] who studied the reaction with Fehling solution. He found, as a mean result of a number of experiments, that 1 gram of uric acid yields cuprous oxide corresponding to 0.800 gram of copper. On the assumption that 1 molecule of uric acid reduces 2 molecules of copper oxide the reduced copper obtained should amount to 0.7556 gram ; the reduction therefore goes a little further than this theoretical relation.

The reducing action seems to be much more readily followed in the ammoniacal solution, however, and several tests were made to establish the relation under such conditions. The following are the details in tabular form :

TABLE IV.—REDUCING POWER OF URIC ACID.

Uric acid in 100 cc. Mg.	Copper oxide taken.	Uric acid solution used. cc.	Uric acid to 130.2 mg CuO. Mg.	Mols. CuO to 1 mol. $C_5H_4N_4O_3$.
80	39.8	36	94.2	2.92
80	65.1	58	92.8	2.96
120	130.2	76.5	91.8	2.99
120	65.1	37.8	90.8	3.03
			Mean,	2.98

The mean result of 1 molecule of uric acid to 2.98 molecules of copper oxide is essentially in the relation of 1 : 3, or 1 molecule of the acid to 1.5 atoms of oxygen absorbed. This is a larger amount of oxygen than corresponds to the reactions usually given for the oxidation of uric acid which is generally

[1] *Ztschr. anal. Chem.*, **35**, 31.

represented as taking place primarily in one of two directions, leading either to allantoin or to alloxan and urea.   These reactions require each one atom of oxygen as follows :

$$C_5H_4N_4O_3 + O + H_2O = CO_2 + C_4H_6N_4O_3$$
$$C_5H_4N_4O_3 + O + H_2O = C_4H_2N_2O_4 + CON_2H_4.$$
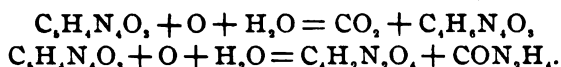
Secondary reactions, however, doubtless take place resulting in the further oxidation of one or the other of these products and using more oxygen.   Thus, from alloxan parabanic acid and other substances may be derived, and possibly are derived in the oxidation in question.   A reaction leading to parabanic acid from the partial oxidation of the alloxan in the above case may be represented in this way :

$2C_5H_4N_4O_3 + 3O + 2H_2O =$
$$2CON_2H_4 + C_3H_2N_2O_3 + C_4H_2N_2O_4 + CO_2.$$
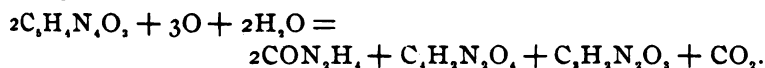
Whether this reaction represents the course of the oxidation or not it remains true that the uric acid takes up more oxygen than is required by the simpler reactions given above.   This is true also of a reaction in sulphuric acid solution referred to below.

Having described the three important substances in urine which exert a reducing action on the ammoniacal copper solution, it remains to explain how the last two mentioned, along with urea and ammonia, the other important products of nitrogenous excretion, were practically determined in the investigation in hand.   The amounts of these last substances are of interest in connection with the actual reducing compounds.

DETERMINATION OF CREATININ.

This body is most accurately obtained by precipitation from the prepared urine in the form of zinc chloride double salt.   This is the method of Neubauer modified by Salkowski, but it is desirable to use as large a volume of urine as possible.   In the work below I used, when available, 480 cc. which was treated with barium hydroxide to faint alkaline reaction and precipitated with barium nitrate in the cold.   In a few cases milk of lime and calcium chloride were used in this preliminary treatment.   The volume was then made up to 600 cc., filtered after half an hour, and of the filtrate 500 cc., representing 400 cc. of the original urine, was taken for the further work.   Care was observed to

secure and maintain a nearly neutral reaction in this liquid so as to avoid, in the following evaporation, the conversion of creatinin into creatin. The final precipitate of the zinc chloride salt was collected on a Gooch crucible, dried at 100°, and weighed. From this weight that of the pure creatinin was calculated and this is given in the table below.

DETERMINATION OF URIC ACID.

Of all the methods now available, the Fokker-Hopkins process seems to give the most regular and trustworthy results. 100 cc. of urine are precipitated with about 30 grams of pure ammonium chloride, or enough to produce a saturated solution. The beaker containing the precipitate is allowed to stand in a cool place over night. Then the precipitate is collected on a filter and washed thoroughly with a saturated solution of ammonium sulphate to remove all chlorine. The filter is perforated and by aid of a jet of hot water the precipitate is washed into a flask. About 100 cc. of the water should be used. To this turbid liquid 20 cc. of pure strong sulphuric acid is added, and then, without delay, twentieth-normal permanganate solution from a burette until a faint pink tinge is secured which is permanent several seconds. For this stage of the reaction Hopkins gives 1 cc. of the twentieth-normal permanganate as corresponding to 3.75 mg. of uric acid. By waiting and adding more permanganate from time to time, as the color fades, a considerably larger volume may be used, for which no factor has been worked out. For the direct oxidation, using 1 atom of oxygen to 1 molecule of uric acid, each cubic centimeter of the twentieth-normal permanganate solution should correspond to 4.2 mg. of the acid instead of 3.75 mg. The results obtained by taking a later reading correspond more nearly to an oxidation with 1.5 atoms of oxygen to each molecule of acid, but they are not definite enough for calculation. The Hopkins factor has therefore been used, and, it is believed, with a considerable degree of accuracy, since numerous blank experiments were carried out with pure uric acid to fix the point for observation of the end color.

DETERMINATION OF UREA.

This has been carried out by the two common methods, the Liebig process by titration with mercuric nitrate, giving properly

a rough measure of the total nitrogen rather than the urea itself, and by the Knop-Hüfner hypobromite or hypochlorite process. The results of the first method are always too high if calculated as urea, while those of the latter are too low. As the last process was carried out it was assumed that 95 per cent. of the urea present was decomposed normally according to the equation

$$CON_2H_4 + 3O = CO_2 + N_2 + 2H_2O,$$

the calculations being made accordingly from the experimental results. The observations were made in a Lunge nitrometer, the gas volumes obtained being always reduced to standard conditions. Even with the various corrections the results were considerably lower than those by the Liebig process because of the inherent positive errors in the latter. Something will be said about this below when the experimental results are discussed.

DETERMINATION OF AMMONIA.

Of all the processes recommended for the determination of the small amounts of ammonia found in urine the most reliable is the old Schloesing method of liberation by milk of lime and absorption by standard acid, under a bell-jar. The urine, about 50 cc., is measured into a glass crystallizing dish and mixed with an excess of milk of lime. Over this dish a glass evaporating dish containing a small known volume of standard sulphuric acid is supported on a triangle. The whole is covered without delay with a clean glass bell-jar, resting on a glass plate and is allowed to stand three days for the liberation of the ammonia, and its absorption by the titrated acid. At the end of the time the bell-jar is rinsed out with a little water which is added then to the dish with the standard acid. This is finally titrated and the loss in acidity measures the ammonia absorbed; while the process is very slow little or no risk is incurred of decomposing urea or other substance containing nitrogen and thus liberating an excess of ammonia. It is, of course, necessary to operate on fresh urine, as the object is to measure that normally present, and not that which may be made by the alkaline fermentation of urea. The results are always a little low, because a small portion of the ammonia escapes either liberation or absorption. To determine the probable error here a number of experiments were made with weak ammonium chloride solutions, corresponding in ammoniacal

strength to normal urine. These experiments gave very concordant results from which it appeared that after three days' time, at the temperature of the tests, 90 per cent. of the ammonia present was liberated and absorbed by the acid. In all the experiments below the results obtained were corrected by the aid of this factor.

Table V, following, gives the result of examinations of a number of normal urines, embracing determinations of the above-described constituents. These urines were collected so as to secure the whole day's excretion and were kept cold until the full twenty-four hour sample was obtained. The analysis was then begun immediately, and finished as speedily as possible. Fifty cc. of the standard copper solution were always employed in the reduction test, and the following table gives the volume of urine required to reduce this under the conditions described above. The reaction of the mixed day's urine was always acid and all samples, except No. 7, were of the usual normal yellow color. This sample was dark, probably because of its concentrated condition. It will be noted that the average total volume is smaller than is usually assumed as the mean daily excretion.

TABLE V.—RESULTS OF URINE ANALYSES.

No. of sample.	Excretion in twenty-four hours.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution.	Ammonia from 1000 cc. of urine.	Uric acid from 1000 cc. of urine.	Creatinin from 1000 cc. of urine.	Urea from 1000 cc. of urine by the Liebig process.	Urea from 1000 cc. of urine by the Knop-Hüfner process.
			cc.	Mg.	Mg.	Mg.	Grams.	Grams.
1	1230	1.031	21.0	645.0	840.0	1930	30.50	....
2	1450	1.035	21.2	522.0	743.0	1876	25.60	....
3	845	1.027	23.6	654.8	832.5	1268	38.80	....
4	1920	1.019	22.5	427.0	646.0	851	25.75	....
5	1950	1.023	20.2	465.0	678.0	1681	24.74	23.72
6	1200	1.025	20.5	593.1	619.0	1195	29.69	27.66
7	765	1.024	18.9	526.6	637.5	961	31.10	27.46
8	1775	1.020	58.0	227.7	....	653	12.90	....
9	1020	1.030	14.9	858.8	971.2	1750	39.18	37.27
10	1280	1.018	27.3	408.0	423.7	1016	17.57	14.83
11	1090	1.024	23.3	631.0	510.0	1374	25.04	24.54
12	1190	1.025	25.6	431.7	611.0	1381	32.72	29.72
13	915	1.025	21.1	711.7	630.0	1604	28.17	25.56

No. of sample.	Excretion in twenty-four hours.	Specific gravity at 20°.	Urine required to reduce 50 cc. of copper solution. cc.	Ammonia from 1000 cc. of urine. Mg.	Uric acid from 1000 cc. of urine. Mg.	Creatinin from 1000 cc. of urine. Mg.	Urea from 1000 cc. of urine by the Liebig process. Grams.	Urea from 1000 cc. of urine by the Knop-Hüfner process. Grams.
14	1440	1.015	27.8	522.0	491.0	868	17.67	15.85
15	1220	1.029	21.2	716.0	671.0	757	26.46	20.94
16	1200	1.025	19.7	711.6	712.5	1735	32.11	31.23
17	800	1.030	17.9	660.0	693.8	1681	34.23	30.29
18	900	1.022	23.7	488.7	581.3	1239	21.91	17.83
19	1100	1.027	18.1	507.7	581.2	1898	26.32	21.73
20	835	1.032	17.1	1001.0	1020.0	1417	39.10	34.68
21	900	1.023	17.4	569.4	626.0	2224	26.63	23.66
22	970	1.026	23.4	374.8	521.0	976	18.61	16.15
23	1600	1.018	28.0	601.6	416.2	926	19.30	17.60
24	1120	1.027	20.7	811.3	701.2	1477	24.55	22.47
Means, 1167		1.025	23.0	602.0[1]	658.7	1392[1]	27.68[1]	24.37

The analytical results as obtained are given in Table V. These, as might be expected, are quite variable, and at first glance do not reveal any relationship that appears characteristic. For better comparison I have stated the amounts of urea, uric acid, ammonia, and creatinin found in grams or milligrams per 1000 cc. rather than for the excretion of twenty-four hours. In Table VI, I have calculated the total reducing power in terms of CuO for 1000 cc. of each urine, and have then done the same for the uric acid and creatinin, basing the calculation on the assumption that under the conditions of the experiments each molecule of uric acid reduces 3 molecules of copper oxide and each molecule of creatinin reduces 2 molecules of the oxide. The sum of these two reductions is given in a separate column, and finally the ratio of this to the total reduction is given in the last column.

[1] No. 8 not included.

TABLE VI.—RELATION OF REDUCING POWERS.

No. of sample.	Total reducing power of 1000 cc. of urine in grams of CuO.	Reducing power of the uric acid in 1000 cc. of urine in grams of CuO.	Reducing power of the creatinin in 1000 cc. of urine in grams of CuO.	Sum of the uric acid and creatinin reductions.	Relation of the uric acid and creatinin reductions to total reduction.
1	6.200	1.194	2.719	3.913	0.631
2	6.141	1.056.	2.643	3.699	0.602
3	5.517	1.184	1.786	2.970	0.538
4	5.787	0.911	1.199	2.110	0.365
5	6.446	0.964	2.368	3.332	0.517
6	6.351	0.880	1.684	2.564	0.404
7	6.889	0.906	1.354	2.260	0.328
8	2.245	....	0.920	....	....
9	8.738	1.381	2.370	3.751	0.429
10	4.769	0.602	1.432	2.034	0.427
11	5.588	0.725	1.936	2.661	0.476
12	5.086	0.869	1.946	2.815	0.554
13	6.171	0.896	2.260	3.156	0.511
14	4.684	0.698	1.223	1.921	0.410
15	6.141	0.954	1.066	2.020	0.329
16	6.609	1.013	2.444	3.457	0.523
17	7.291	0.986	2.369	3.355	0.460
18	5.494	0.826	1.746	2.572	0.468
19	7.192	0.825	2.674	3.499	0.487
20	7.614	1.417	1.997	3.414	0.448
21	7.483	0.890	3.133	4.023	0.538
22	5.564	0.741	1.375	2.116	0.380
23	4.650	0.592	1.305	1.897	0.408
24	6.290	0.997	2.081	3.078	0.489
Means,	6.204	0.935[1]	1.961[1]	2.896	0.466

From the mean values given at the foot of the last table several interesting relations may be established. As in the ammoniacal solution 1 molecule of dextrose reduces 5.88 molecules of copper oxide, the above average reduction corresponds to 2.836 grams of sugar per liter, or about 0.28 per cent. The uric acid amounts to 0.658 gram per liter, or 0.065 per cent. The creatinin is equivalent to 1.392 grams per liter or 0.136 per cent. The data of the last column show that a large portion of the total reduction is due to the action of these latter products.

[1] No. 8 not in averages.

This, in the mean, amounts to 46.6 per cent., which calculated as sugar is equivalent to 1.322 grams per liter, leaving 1.514 grams as the amount of sugar possibly present. This, however, represents a maximum value, as there are unquestionably traces of other bodies present which, like the uric acid and creatinin, exert a reducing action. If the effect of these could be estimated it is likely that the reducing power, in the mean, would be found to be pretty evenly distributed between the saccharine and non-saccharine products.

It is not possible to draw any very exact general conclusions from the figures of the above table connecting the numerical values with the character of the food of the individual or with any other factor. Most of the urines were obtained from young men, students or teachers, and all pretty well nourished. It may be noticed, however, that the urines showing the highest reduction ratio for uric acid, and creatinin, as compared with the total reduction, were from men with the strongest physique with a diet containing much meat. On the other hand the lowest uric acid, and creatinin reductions correspond to cases of slighter physique and lower nutrition. Urines Nos. 1 and 2 were from a man consuming a diet largely of meat. No. 15 was from the same individual some weeks later after a change of diet to bread and vegetables largely. But from most of the urines no characteristic relation is apparent; another series of investigations is in progress in which the question of food in relation to the reducing power is being more closely determined.

RATIO OF UREA TO URIC ACID.

This ratio is more important and more characteristic than is the absolute amount of the acid. In the older works on urine analysis or physiological chemistry it was always stated too high, and usually as 50 : 1 or 60 : 1. This is due to the fact that the amount of uric acid was generally underestimated, while that of urea was naturally overestimated if found by the Liebig process, and not corrected.

In making an examination of a fraction of the day's excretion, instead of on the mixed twenty-four hour sample, a false ratio is also usually found because the urea and uric acid are not eliminated at a constant rate following ingestion of food. The ratio

from the above table is 36.9 : 1 if we consider the urea as measured by the Knop-Hüfner process and 42 : 1 if we take the uncorrected values for urea as found by the Liebig process. The results here are in the mean about 10 per cent. high as may be shown when we take into consideration the effect of the other nitrogenous bodies, especially the ammonia, uric acid, and creatinin, on the mercuric nitrate solution. With such a correction subtracted the amount of urea approaches closely that found by the gas volume method and the ratio becomes again about 37:1; this result is in accord with the average normal ratio as found in experiments on the excretion of the twenty-four hours as made by Hopkins and others. See an interesting paper by Hopkins and Pope[1] in which variations in the excretion of urea and uric acid in relation to kind of food and time of meals is dis- cussed.

THE AMOUNT OF AMMONIA.

The ammonia in 1000 cc. of urine, as shown by the above figures, is, in the mean, 602 mg., but the individual varia- tions are between 228 and 1001 mg. These correspond roughly to the variations in the other nitrogen bodies. The average daily excretion is seen to be 703 mg. The daily extremes are 364 and 908 mg. The average correction to be applied to the Liebig urea titration on account of the ammonia present is about 1.2 cc. of the usual standard mercuric nitrate solution. This re- sult was found in experiments carried out on the titration of urea solutions containing small amounts of added ammonia, and is somewhat lower than the factor given by Feder.[2] Experiments are now in progress to determine more definitely the behavior of uric acid and creatinin in this titration, the statement in Neu- bauer and Vogel's Harnanalyse[3] requiring, apparently, a slight correction.

THE DAILY AVERAGES.

The numbers above given are expressed, for convenience in comparison, in grams or milligrams per liter. The values for the daily excretion are often interesting and these will now be given as calculated from the volumes collected in the twenty-

[1] *Journal of Physiology*, 23, 271.
[2] Neubauer and Vogel's Harnanalyse, 9th German edition, p. 519.
[3] *Loc. cit.*

four hours as shown by the figures of the second column in Table V.

TABLE VII.—MEAN RESULTS FOR DAILY EXCRETION.

Volume excreted ························ 1167.00 cc.
Total reduction, equivalent to ··········· 3.31 grams $C_6H_{12}O_6$.
Uric acid and creatinin reduction equiva-
   lent to ·························· ···· ···· 1.54   "   "
Remaining reduction equivalent to······ 1.77   "   "
Amount of ammonia····················· 0.703 gram.
Amount of urea (mean of gas method and
   Liebig, corr.) ······················ 29.75 grams.
Amount of creatinin···················· 1.624 "
Amount of uric acid··················· 0.799 gram.

The urines examined in the above experiments were all normal and represent the excretion from average meat and vegetable diet. In a following paper I will give results obtained from urines of consistent vegetarians, noting the same relations. Most of the experimental work detailed above was done by Mr. Frank Wright, assistant in the laboratory of physiological chemistry, and Mr. Charles Ericson, to whom my thanks are due.

NORTHWESTERN UNIVERSITY,
   CHICAGO, April 24, 1900.

AN EXAMINATION OF BROWN AND TAYLOR'S OFFICIAL METHOD OF IDENTIFYING BUTTER.

BY JOHN A. HUMMEL.

THE recent great increase in the production of renovated butter, due probably to the improvements in the method of its manufacture and the prevailing high price of creamery butter, has necessitated, in several states, the enactment of laws regulating its sale. Since the enactment of these laws there has been some discussion as to reliable methods for its identification. The fact that the chemical properties and the proximate composition of samples examined are entirely within the range of normal butter, has directed attention to its physical properties more particularly its behavior with polarized light. As is already well-known, in the manufacture of renovated butter, the butter-fat is melted and then cooled rather rapidly in a stream of cold water. This melting and rapid cooling induces a semicrystallization of

the fat.   It was thought that this fact might be taken advantage
of and would at least deserve some study.   For the experiments
carried on in this laboratory fifteen samples of renovated butter
secured from factories in St. Paul, Minneapolis and Duluth were
used; as many samples of undoubted normal butter from Minne-
sota creameries and dairies were also examined.   The prepara-
tions for the microscopic examination were made by simply
placing a small bit of the butter on a glass slide and pressing it
into a thin film with a cover-glass.   The preparation was then
immediately examined with a polarizing microscope giving a
magnification of 120 to 150 diameters.   A selenite plate was
placed between the slide and the lower nicol.   In every case the
normal butters gave with the selenite which was used a uni-
formly blue colored field, showing the entire absence of fat crys-
tals.   The renovated butters on the other hand gave a blue
field mottled with yellow; this mottled appearance varied
slightly in intensity but was very marked and distinctive in
every case.   The accompanying photomicrographs are from
representative preparations and are believed to be fair averages.
In making these photomicrographs the selenite was not used,
the thin film of butter being simply placed between crossed
nicols.   The source of light was a 16 candle-power incandescent
electric light, and an exposure of fifteen minutes was necessary for
the normal butter, eleven minutes for the renovated butter, and
eight minutes for the oleomargarine, using plates of medium
rapidity.

The writer is well aware of the severe criticism directed against
the method proposed by Dr. J. Campbell Brown, and later by
Dr. Taylor, for identifying adulterated butter by means of the
microscope and polarized light, yet he has found a microscopic
examination of great value, and believes it to be one of the best
methods for the identification of renovated butter, as found upon
the Minnesota markets at least.   In the course of work in this
laboratory 247 samples of butter have been subjected to a micro-
scopic examination as outlined above and out of this number 58
showed conclusive evidence of having been melted and cooled
as in the process of renovating.   A majority of those samples
which could be traced to the manufacturers were admitted as
being renovated and some fines have been imposed.
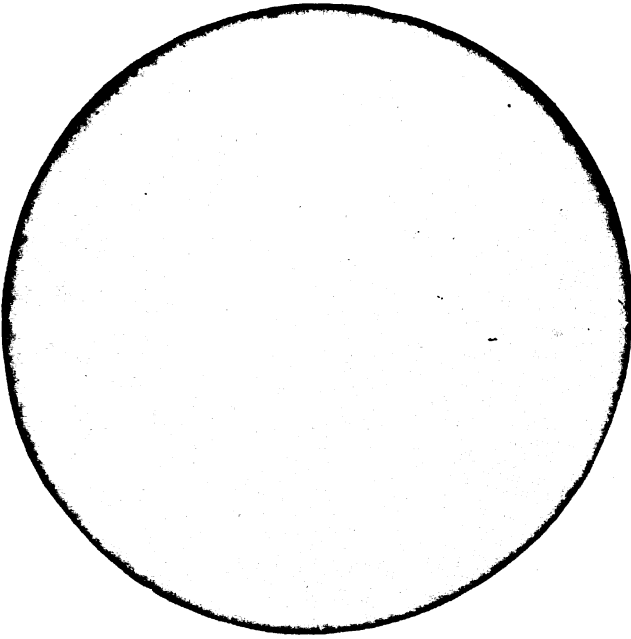
Fig. 1.—Normal Butter.
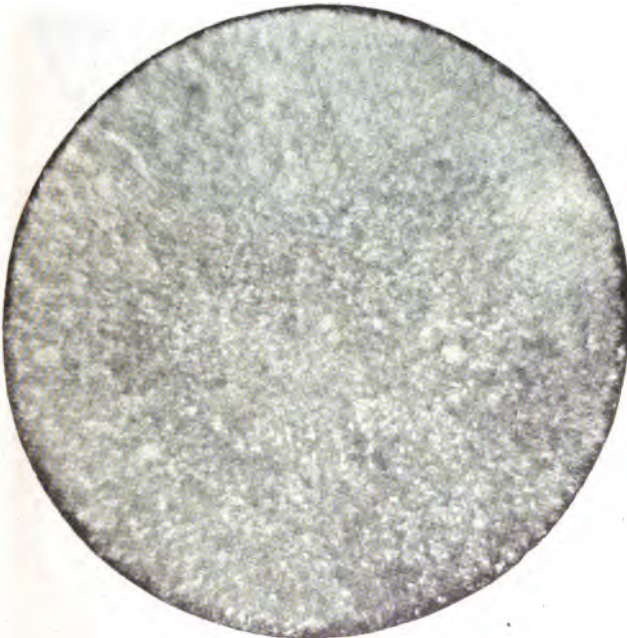
Fig. 2.—Renovated Butter.
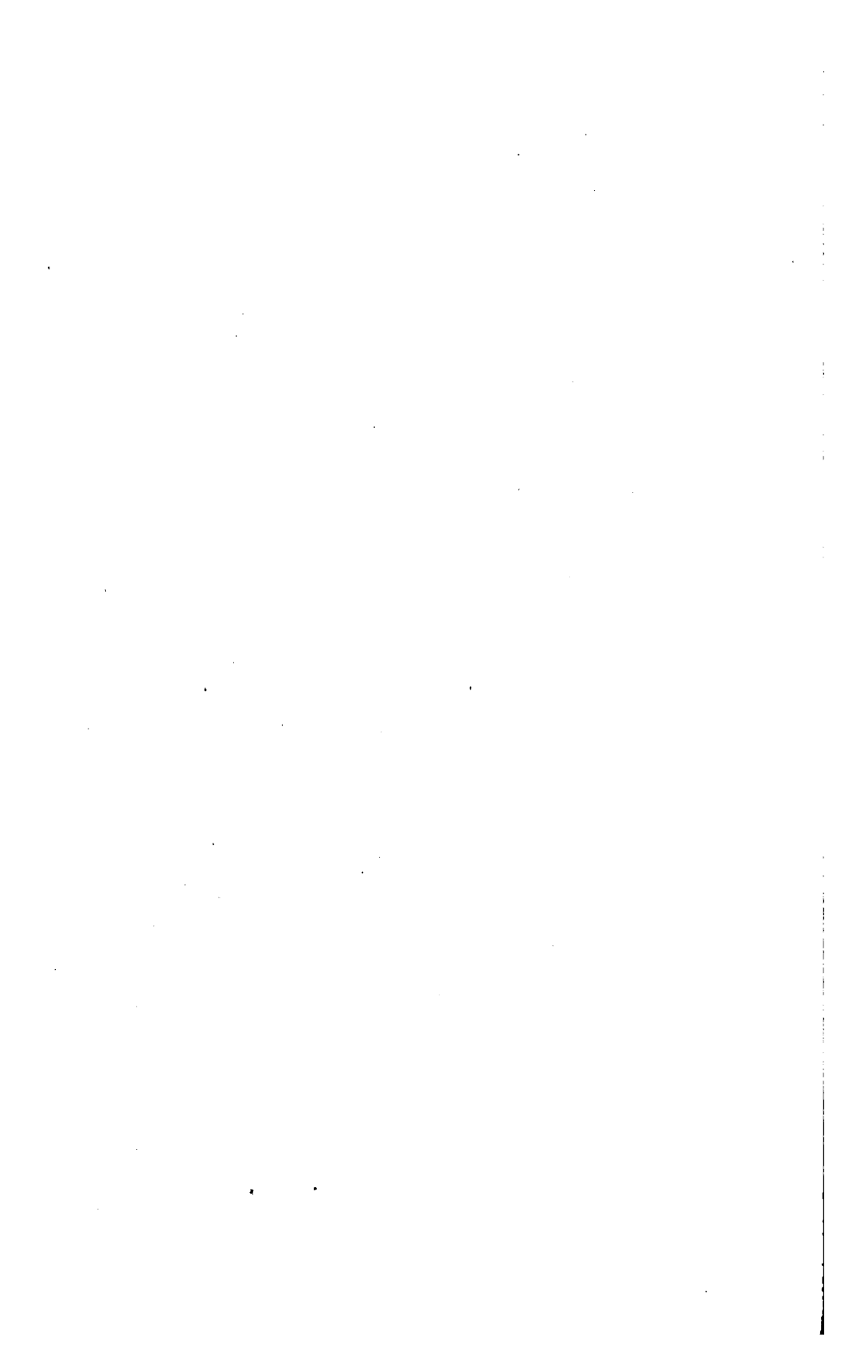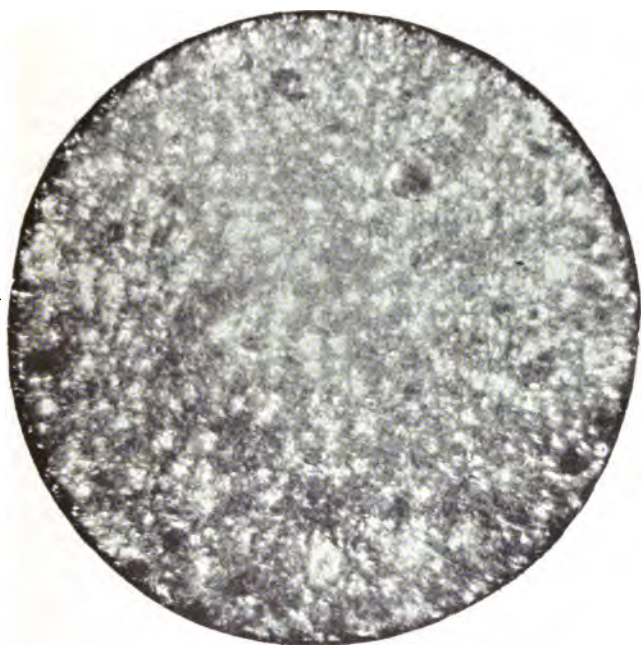
Fig. 3.—Oleomargarine.

In the examination of these samples the greatest reliance was placed in every case on the microscopic appearance, though other tests were also used.

LABORATORY OF THE MINNESOTA STATE DAIRY AND FOOD COMMISSION.

ON THE PREPARATION OF NUCLEIC ACIDS.[1]

BY P. A. LEVENE.
Received April 14, 1900.

THE various modifications of Altman's and Kossel's methods of obtaining nucleic acid, which have appeared during the last year clearly demonstrate two facts: first, that the old methods were unsatisfactory; and secondly, that a thorough knowledge of the nucleo compounds is of ever-increasing importance to all investigators in the field of the chemistry of the cell.

All the new methods published in recent years are based on two properties of the nucleic acids; namely, their solubility in acetates and their resistance to dilute alkalies on heating. Both properties were observed only by the authors of the new methods. The improvement recently advocated by Schmiedeberg was based on the idea of removing (by means of copper salts) the proteid material which combines with the nucleic acids, to form the nucleo-compounds occurring in cells and tissues.

One of the properties of the nucleic acids described by the more recent investigators, namely their resistance to heating with alkalies, stands in contradiction to the observations of the older workers. Thus Miescher considered it requisite that the material which was being treated for nuclein should be kept at a very low temperature during every phase of its preparation. Kossel has succeeded in decomposing the ordinary nucleic acid of the thymus into thymic acid by heating it in water on the water-bath.

Neuman, advocating the heating method with alkalies, states that by this method more than one acid is generally obtained. From the fact that different proportions of the acids vary with the duration of heating, he draws the conclusion that the three acids are modifications of the one occurring in the tissue.

[1] Read before the New York Section of the American Chemical Society, April 6, 1900.

Hammarsten and Bang, who have applied the method of heating with alkalies for obtaining their guanilic acid, obtained a substance with properties differing greatly from those of all the other acids hitherto described.

Thus from the statements of the investigators advocating the "hot" method it may be admitted that the new methods, being an improvement over the old ones, they may be still further perfected, because they do change somewhat the original character of the substance.

In addition to this, I would like to add that to some nucleo-compounds the new method cannot be applied at all, as their decomposition on heating with very dilute alkalies takes place in so short a time that it is impossible to obtain any satisfactory yield by that method. I refer to the compounds known as para-nucleo-compounds.

A uniform method for obtaining all the nucleic acids is, however, most desirable. During the last two years I have been engaged in the study of different nucleo-compounds, and I have used, with satisfactory results, a method differing from those used by other authors. Fresh tissues, nucleo-proteid, as well as para-nucleo-proteids are treated with a strong solution of alkalies (5 per cent. sodium hydroxide or 8 per cent. ammonia), and allowed to stand in a cool place one to two hours. This solution or mixture is then gradually and slowly neutralized with acetic acid, care being taken not to add too much acid at a time, so that the temperature of the solution does not rise too high. It is advisable to keep the solution in a cooling mixture or to add ice to the alkaline mixture itself. When the mixture remains only slightly alkaline a saturated solution of picric acid is added until the mixture becomes neutral or nearly neutral (about 75 cc. of the picric acid to 1 liter of the mixture is generally sufficient); more acetic acid is added until the mixture is rendered strongly acid and then allowed to stand for some time, filtered, and to the filtrate is added 95 per cent. alcohol until the latter ceases to form a precipitate. This precipitate is nucleic acid. The picric acid is added in order to remove the proteid material. On neutralization with acetic acid a sufficient quantity of acetates is formed to enable the precipitation of all the nucleic acid by means of alcohol. (In the absence of acetates nucleic acid cannot be pre-

cipitated by alcohol.) By this method I have treated ovovitellin, ichtulin of cod-fish eggs, cod-fish sperm, pancreas and bacillus tuberculosis.

The very crude acid obtained from the ovovitellin contained 9.65 per cent. of phosphorus; three other samples purified contained, 10.02, 9.95, and 9.79; a copper salt contained, P, 8.57, and Cu, 12.36 per cent.; for the free acid, P = 9.78 per cent. The acid obtained from the same vitellin by Milroy in Kossel's laboratory varied in its contents of posphorus from 7.51 to 7.94 per cent. The acid obtained from ichtulin contained 8.46 per cent. of phosphorus. Walter, who studied the chemical nature of ichtulin in Kossel's laboratory, failed to obtain from it a substance similar to nucleic acid. The acid obtained from the cod-fish sperm was biuret free after the first precipitation and contained 8.65 per cent. of phosphorus. From the pancreas an acid was obtained with the same solubility as the other nucleic acids, while the substance described by Bang as guanilic acid differed in that respect from the other nucleic acids. From the bacillus tuberculosis the acid was also obtained biuret free after the first precipitation.

The study of the chemical properties of all the above-mentioned acids is now in progress.

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A CHROMIUM CELL FOR THE RECTIFICATION OF ALTERNATING CURRENTS.

BY J. LIVINGSTON R. MORGAN AND W. A. DUFF.

MUCH attention has been given of late to aluminum rectifying cells. These consist of a platinum and an aluminum electrode in a solution of sulphuric acid or potash alum. When

the current is applied to such a cell, the aluminum electrode being the anode, the aluminum plate becomes covered with a highly resistant film which prevents, to a great extent, the further passage of the current in this direction. In the opposite direction however, *i. e.*, from platinum to aluminum through the liquid, the resistance of the electrolyte alone is encountered. If an alternating current is applied to such a cell, keeping the voltage down below a certain minimum point, an interrupted current, made up of the half waves of the alternating one, is the result. If the alternating voltage is increased gradually a point is finally reached at which the resistance of the film is overcome and the latter broken down after which the alternating current goes through unchanged. Up to this breaking-down point the current becomes less and less asymmetrical ; *i. e.*, the opposite half waves become more and more alike in size. The minimum electromotive force which will cause the film to break down has been found by us as well as by others to be about 26 volts.

Our experimental work on this subject was done in the early part of 1899, but as it was not published at the time most of our results have since been found and published by others. The substitution of chromium for aluminum, however, has not yet been reported so that we propose to give our results very briefly here. At the time we did not expect to find any connection with the work of Hittorf[1] on chromium, but since such a one has been found we deem the result worthy of a short description for its bearing upon the general behavior of metallic chromium. Since our work was suspended in April, 1899, the results are fragmentary but we think of their kind, conclusive.

The electrolyte used throughout was 10 per cent. sulphuric acid. The chromium electrode consisted of a fragment of the chemically pure metal[2] fused into a glass tube containing mercury by which the connection was made. The platinum electrode was made of a strip of foil. The apparatus consists simply of a graded source of direct current, the amount going through the cell being measured by a low reading ammeter (0—5). A reversing switch is also used by which either the chromium or platinum may be made the anode. If the platinum

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[1] *Ztschr. phys. Chem.*, 25, 729, and 30, p. 481.
[2] Eimer and Amend.

is first made the anode, the solution becomes yellow, and hydrogen gas is given off at the chromium electrode. If the chromium is now made the anode we find that no current goes through the cell, while when the platinium is the anode the current passes freely. We have then an asymmetrical resistance. *Using the chromium as anode and increasing very gradually the impressed electromotive force it is possible to stop any current entirely, as far as readings on the ammeter are concerned, until the pressure of about 75 volts is reached.* It is not difficult to stop this amount after the cell has once stopped it, but in starting, if the increase is made too rapidly, the current will force its way through. Of course, with the platinum as anode the resistance offered is only that of the sulphuric acid, so that the current is rectified with great efficiency.

When the increase in the electromotive force is made so rapidly that the current goes through from chromium to platinum, or after the cell breaks down by the application of more than 75 volts, a very peculiar result is obtained, and it is by this that Hittorf's results for the "active" and "inactive" states of chromium are confirmed. *Unlike the aluminum cell after it has broken down the chromium cell is still an asymmetrical resistance, but only when the platinum plate is made the anode. With chromium as the anode the current now passes freely.*

If in this condition the cell is broken down by the application of too high an electromotive force to the platinum anode another reversal takes place so that about 75 volts can again be stopped using the chromium as anode. The electromotive force necessary to cause this second reversal does not seem to be fixed, but the reversal always takes place. This change in the behavior of chromium is doubtless due just as were Hittorf's to the change from the "active" to the "inactive" state, and the change can be well shown experimentally in this way.

One other thing, we think, is proved by this work. Since chromium and aluminum act very much alike chemically, we should expect that they would both act asymmetrically in a cell and for the same reason. Aluminum has been supposed to act by a resistant layer of an oxid[1] and since chromium, when used in the same way, causes a reversal of the asymmetrical effect and

[1] Norden: *Ztschr. Elektrochem.*, 6, 159 and 188.

according to Hittorf its "active" and "inactive" states are not caused by resistant films, hence the asymmetrical effect of aluminum can only be caused by these ; so that the theory of the action of the aluminum cell, as due to the formation of a resistant film, is confirmed.

REMARKS ON SOME METHODS OF DETERMINING CARBON IN STEEL.[1]

BY GEORGE AUCHY.

IN Blair's "Chemical Analysis of Iron"[2] it is stated that combined carbon in steel can be determined by loss upon ignition, 70 per cent. of the loss representing the carbon. As Blair gives the percentage of carbon in the carbon sponge as "about" 70 per cent., and as the method is not in general use, it may be inferred that it is known to be inexact. Mr. George Dougherty, in the *Iron Age* for May 11, 1899, proposes a method which is identical except that the carbon sponge is washed four times with hot nitric acid (sp. gr. 1.13) to dissolve out copper and copper sulphide. It may be questioned whether this procedure makes the method an accurate one as Mr. Dougherty's article does not throw much light on this point (only one result being given). Some experiments were made by the writer, which showed that, on the contrary, the washing with hot nitric acid is itself a source of error in one particular, and a possible source of error in another. 1. The hot nitrc acid dissolves some of the carbon, and the amount dissolved varies with different steels. 2. The carbon sponge absorbs and retains a portion of the nitric acid, and this absorption is possibly not uniform in all cases. That the washing with hot nitric acid (sp. gr. 1.13) four times dissolves out carbon, and in varying amount, is shown in the following results, all from different steels:

1 Read at the February Meeting of the Philadelphia Section.
2 Blair's "Analysis of Iron," second edition, p. 151.

By combustion as usual. Per cent.	By combustion but washed with hot nitric acid. Per cent.	Percentage of loss	Carbon sponge boiled up or digested with hot nitric acid.
1.078	1.03	4.45	....
0.76	0.76	0.00	...
0.715	0.68	4.90	....
0.72	0.697	3.20	....
0.81	0.775	4.32	0.628 (Boiled up.)
0.665	....	....	0.62 (Digested one-fourth hr.)
0.665	....	....	0.56 (" two hours.)

Eleven other similar results were obtained in which the lowest percentage of loss was 2.15, and highest 5.74. On digesting a carbon sponge with hot nitric acid (sp. gr. 1.13), and filtering the filtrate after boiling to expel lower oxides of nitrogen, decolorized permanganate solution.

That the carbon sponge, when washed with hot nitric acid (sp. gr. 1.13), absorbs and retains nitric acid, is indicated by the following results :

No.	Weight of carbon sponge. Washed as usual. Gram.	Weight of carbon sponge. Washed twice with hot hydrochloric acid; six times with hot water; four times with hot nitric acid; and lastly ten times with hot water. Gram.
723	0.0856	0.0955
691	{ 0.0583 0.0583	0.0647
723	0.0856	0.0880
739	0.0654	0.0747
740	0.0674	0.0742
BG2	0.0603	0.0750
737	0.0679	0.0740

No effort was made to ascertain whether the absorption was uniform in all cases. Instead the following determinations were made with a view to ascertaining the average percentage of carbon in the carbon sponge[1] and also at the same time the range of error in the process.

[1] Mr. Dougherty gives the percentage as 0.6750. This does not represent the absolute percentage of carbon in the nitric acid-washed carbon sponge, but the absolute percentage, plus the loss of weight, in terms of carbon, suffered by the paper disk in being washed by acid liquids, plus the loss in weight through the solubility of the carbon in the hot nitric acid wash. Nor does the writer's average factor (0.6000) represent the absolute percentage of carbon in the carbon sponge, but the percentage plus the loss by washing with hot nitric acid. The writer's filtrations were made through asbestos.

No.   1012   1013   1014   1015   1016 1017 Standard

Factor $\begin{cases} 0.6319 \\ 0.6333 \end{cases}$ $\begin{cases} 0.6415 \\ 0.5845 \end{cases}$ $\begin{cases} 0.5950 \\ 0.5898 \end{cases}$ $\begin{cases} 0.5698 \\ 0.5897 \end{cases}$ 0.5976 0.5575 0.6044 Average 0.6000

From the above it is seen that in a 0.60 per cent. carbon steel, results by this method might vary from 0.557 per cent. to 0.641 per cent. carbon, taking 0.6000 to be the factor. In the above tests only two washings with hot nitric acid (sp. gr. 1.13) in each case were made, in the lower row of tests, and three in the upper row to reduce the error from this cause as much as possible. The steels used were Swedish band saws containing not over 0.008 per cent. sulphur. If Meineke is right in considering the sulphur of the steel to be present in the carbon sponge in the free condition,[1] another source of error must be counted against the process when used for high sulphur steels.

THE USUAL COMBUSTION METHOD.

Professor D. H. Browne,[2] in describing the apparatus for the moist combustion method, says: "It is very necessary to have a small U-tube containing $CaCl_2$ in one leg and soda-lime in the other attached to the potash bulbs and weighed with them. The small straight tube designed to contain $CaCl_2$ attached to the potash bulb is not sufficient to prevent the escape of a slight quantity of water from the potash solution." Mr. A. A. Blair, in using the dry method, found that the calcium chloride tube did not absorb all the moisture drawn over from the potash bulb.[3] Mr. J. M. Camp, of Carnegie Steel Co., considers it necessary to have a weighed potash bulb containing strong sulphuric acid attached to the calcium chloride prolong.[4] The writer of this article several years ago described to this Society some experiences of this kind in using the wet method of combustion. The carbon dioxide was not completely absorbed by the potash solution (sp. gr. 1.27), and the moisture not completely retained by the prolong and drying train; the amount of moisture not retained by the drying train and passing into the potash bulb amounting to about 0.065 per cent. in terms of carbon with two sets of bulbs and prolongs in use, was 0.045 per cent. for the first set usually, and 0.02 per cent. for the second, and a correction to this amount

[1] *Ztschr. angew. Chem.* (1888), 376.
[2] *J. Anal. Appl. Chem.*, 5, 338.
[3] *Ibid.*, 5, 128.
[4] "Methods of Iron Analysis."

had to be made in each result. Professor Arnold also in his experience found a correction of 0.045 per cent. (using one bulb) to be necesssary.[1] Professor Chas. F. Mabery found a loss of moisture and suspected a loss of carbon dioxide.[2] This seems to be sufficient evidence that the usual drying and absorbing agencies are inefficient. On the other hand, many chemists using both methods of combustion, have, like Dr. Drown, satisfied themselves by actual trial of the efficiency of their apparatus in this respect. The writer himself upon changing to the dry method found no further difficulty of this kind of any great consequence[3] except at first due to the copper oxide being packed into the preheating furnace too tightly, and aspiration being made by the pump. Mr. Buck, of the Bethlehem Steel Co., and Mr. Sargent, of the Carpenter Steel Works (the former with a Shimer apparatus, the latter with a modified oxygen apparatus), use extremely rapid rates of aspiration (allowing only twenty minutes for a combustion) without loss, either, of carbon dioxide or of moisture. Yet it is certain that those of us who have experienced a lack of efficiency of this sort have not simply dreamed or imagined it. What, then, is the reason that the potash solution sometimes fails to absorb all the carbon dioxide, and the calcium chloride or strong sulphuric acid fails to absorb all the moisture? Some recent experiments by the writer suggest an explanation and indicate a source of error, which though very simple may easily be overlooked. This source of error apparently lies in the fact that when there is undue resistance to the passage of gas through the apparatus for any reason, usually because of the calcium chloride or copper oxide having become clogged up in use, or having been packed in too tightly, or too finely divided in the first place, the gas then bubbles through the potash solution and the strong sulphuric acid, and passes through the calcium chloride not evenly and regularly but the reverse, and although precisely the same volume of gas may pass through as in normal conditions, the contact of gas with drying and absorbing materials is obviously less than normal.

[1] "Steel Works Analysis." Professor Arnold thinks this due to something generated in the combustion flask, but the writer obtained the same result by simply aspirating air through the apparatus for the same length of time.

[2] This Journal, 20, 510.

[3] Some moisture escaped from the prolong after being in use a number of tests, but this is now believed to be due to a cause that will appear later on.

This irregularity of action and accompanying loss may be due simply or mainly to the size and shape of the potash bulb, or may have its origin in the oxygen cylinder; but whatever the cause it seems to be a fact that when the gas does not pass freely and easily through the apparatus, and does not bubble evenly and regularly through the bulbs, loss ensues if a rapid or moderately rapid flow be allowed.

The experiments were as follows:

No	Prolong clogged up. Carbon. Per cent.	Prolong in good condition. Carbon. Per cent.
1012	0.715	0.76
1013	0.68	0.716
1015	0.705	0.718

In the last experiment with clogged prolong the rate of speed of gas flow was diminished. With fresh calcium chloride in the prolong the following tests were made. The loss was believed to be due to the resistance offered to the passage of the gas by the 3 inches of rather closely packed copper oxide in the combustion tube.

Steel "S," usual rate. Carbon. Per cent.	Steel "S," slower rate. Carbon. Per cent.
1.053, 1.066, 1.06	1.078, 1.076, 1.077
1.067, 1.07, 1.065	....

The first result under "usual rate" is not the writer's, but that of another chemist, and may perhaps be taken as an indication of some impediment to the flow of gas in his apparatus also. These results and the preceding ones seem to show that it is highly important to have the gas pass through the apparatus freely and easily if it is desired to maintain a rapid or moderately rapid rate of gas flow. Using another apparatus (a Shimer apparatus) in which the flow of gas is very free and unobstructed, no higher results could be obtained by using a slow rate than by using a rapid rate of gas flow. With the first-mentioned apparatus the writer now uses a rate of one bubble per second through the first or purifying bulb for one-half hour followed by ten minutes of a faster rate, and believes this rate slow enough not only to counteract the density of the copper oxide but also to allow for any clogging up of the calcium chloride that may occur; but this slow rate is, of course, impracticable where many combustions have to be crowded into

a day, or when a combustion must be made in the very shortest possible time; when a rapid rate. is employed it would seem imperative to be sure that the gas passes freely and easily through the apparatus, and bubbles regularly and evenly through the potash bulbs. Calcium chloride sometimes clogs up and strong sulphuric acid seems preferable. The writer believes that for the calcium chloride prolong, one could profitably substitute diminutive bulbs for strong sulphuric acid of the Geissler type but constructed to hang instead of to stand so as to allow of being weighed along with the potash bulbs by being suspended from the hook of the balance.

These experiments perhaps throw some light on the cause of the losses of carbon dioxide and moisture experienced by the writer in using the wet method of combustion. Possibly these losses were caused by some stoppage in the apparatus or irregularity of gas flow. As a matter of fact the aspiration (which took place from beginning to end of the process) was made by a filter-pump which the writer has frequently observed does not exert an even and regular suction. Possibly all such losses are attributable (the drying and absorbing materials not being too long in use) to some such cause—perhaps a clogging up somewhere in the apparatus causing an irregular and jerky gas flow; or perhaps too much apparatus, causing, by its resistance, an uneven flow.

Dr. P. W. Shimer has greatly simplified the dry combustion apparatus and his apparatus will, without doubt, eventually altogether displace the old form. He also makes a notable change in the direction of greater simplicity—in the drying and purifying train. A train which vies with Shimer's for simplicity is that of Prof. Arnold's described in his book, "Steel Works Analysis," but in other respects there is a remarkable difference between the two. Shimer's train: cold water for HCl and Cl; calcium chloride for drying; Arnold's train: chromic acid solution for SO_2; concentrated sulphuric acid for drying. It is seen that the difference is fundamental. The former is based upon the belief generally prevalent among American chemists that hydrochloric acid or chlorine, if present in the carbon sponge, is not absorbed by the copper oxide but passes out of the combustion tube, while sulphur dioxide is believed to be converted into sulphur trioxide in the pres-

ence of the glowing copper oxide and absorbed by it. Prof. Arnold's belief is the exact opposite of this; namely, that hydrochloric acid and chlorine are absorbed by the copper oxide of the combustion tube (p.40), and that sulphur dioxide escapes therefrom unchanged. Which theory is correct? That hydrochloric acid, if present in the carbon sponge, is not absorbed by the copper oxide, and does pass out of the combustion tube may easily be proved by testing the water of the Shimer absorption tube after a number of determinations have been made. On the other hand, as proof that sulphur dioxide passes out of the combustion tube, Arnold mentions an experiment in which potassium permanganate solution, placed after the combustion tube and connected with it, became decolorized by the gas. The writer finds that in using Arnold's chromic acid solution immediately following the combustion tube, as he directs, the chromic acid becomes entirely reduced, and the color of the solution changed to green after a considerable number of combustions have been made. But that this reduction is effected by hydrochloric acid,[1] and not by sulphur dioxide, is believed to be proved by the fact that when a bulb containing cold water is interposed between the combustion tube and the chromic acid bulb, the color of the chromic acid solution does not change; nor does the water of the bulb preceding show any trace of sulphur dioxide when tested with permanganate solution. If traces of the gas ever escape absorption by the copper oxide, Shimer's cold water tube would seem to be an ample safeguard. But as a further precaution, concentrated sulphuric acid, saturated with chromic acid, may be substituted for calcium chloride in the train.

The fact observed in the examination of Dougherty's method, of the carbon sponge being slightly soluble in hot nitric acid, suggested the suspicion that it might also be soluble in hot acid double chloride solution to some extent. The following tests were made on the same sample of steel:

Hot double chloride solution. Carbon. Per cent.	Cold double choloride solution. Carbon. Per cent.
1.052, 1.050, 1.06	1.076, 1.078, 1.077

In these tests the double chloride solution was heated (after

[1] Five drops (and probably less) of hydrochloric acid will completely reduce 10 cc. Arnold's chromic acid solution in the cold, standing over night.

solution of precipitated copper was nearly complete) for an hour or more, giving a much severer test of the solubility of the carbon than would occur in actual practice. It may therefore be inferred that the error from this cause in actual practice is very slight or in some cases nothing, for as the second result of the first table of results in this article shows that the carbonaceous residues from some steels are unacted on by hot nitric acid, so it is probable that such residues resist the slightly solvent action of hot double chloride solution. On the other hand, some residues may be much more soluble in hot double chloride solution than those of the above table. The point brought out by these results is merely that heating the double chloride solution of the drillings is attended with some risk of loss.

The carbon residue of the first table, that was not acted on by hot nitric acid was from a saw—a much-worked product. The carbon residues from such finished products seem different from those of ingot steels inasmuch as they give much darker shades to nitric acid in the color test than do the latter; thus, for instance, a 1.07 per cent. carbon steel in a finished saw gave 1.27 per cent. by the color test using a hammered slab as standard.

In washing the carbonaceous residue with hydrochloric acid it is perhaps safer to have the acid cold.

In carbon determinations, the error from moisture condensation in damp weather is well known. In a communication to the Society nearly two years ago the writer gave the results of experiments made in very damp weather which indicated the error from this cause to be usually 0.02 per cent. or 0.03 per cent., and occasionally as high as 0.05 and 0.06 per cent. When these experiments were made it was the writer's habit to have the balance-room door open; this door led into a small ante-room the door of which, at that time, also stood habitually open on account of warm weather, so that the outside air had access to the balance-room. For a long time back, however, the balance-room door has been kept closed, at least during the progress of combustions, and no such excessive condensation as 0.05 per cent. and 0.06 per cent. have occurred, using extra bulbs as an indicator. It is therefore believed to be well to keep the balance-room closed, at least in warm weather when adjoining parts of the laboratory are open. This is, of course, not an absolute

preventive.   Moisture condensations equivalent to something
under 0.02 per cent. carbon may easily occur.

THE COLOR METHOD.

The color method for high carbon steels is generally regarded
with much distrust.   Mr. Wm. Metcalf in his book, "Steel",
says: "For in high carbons the color test in the best hands is
only the wildest guess work."   It is the writer's experience that
the same drillings, even when dissolved at the same time, fre-
quently do not give the same shade, and that by performing the
test in the usual way, results as high as 0.10 per cent., or even
higher, wide of the truth are often obtained.   If the usual
method be elaborated as follows, results not further from the truth
than 0.03 per cent. (usually 0.01 or 0.02 per cent.), or at most
0.04 per cent. can uniformly be obtained : Duplicate tests of
standard and samples are weighed out.   Besides the standard,
duplicate tests of two other steels in which the carbon
has been accurately determined by combustion are also
weighed out.   In the absence of such steels, six samples
of the standard are taken.   When the color comparisons are
made, the two steels of known carbon content are first tested,
and from these tests is averaged a correction to be applied to all
the results subsequently obtained.   When these tests are fin-
ished the second sample of the standard is taken, the correction
found as before, and the testing of the samples duplicated, and the
average of these duplicates taken.   These precautions are simple
and obvious but are of no avail in the presence of a difficulty
which, although it happens very rarely, still does happen.
This difficulty is a carbon color showing a *much* deeper shade
placed to the left of the standard than to the right of it, and
requiring a further dilution equivalent to about 0.10 per cent.
carbon to make the shade to coincide with the standard, the
color when placed to the right showing no change by this
dilution, and still agreeing with the standard.   The result is
then too high by just the amount represented by this extra
dilution, or about 0.10 per cent., and it is necessary, therefore,
when this abnormal shade is noticed, to discontinue the dilution
and to take the reading when the color at the right coincides,
ignoring the left-hand shade altogether.

	As usual. No Carbon. Per cent.	Left-hand shade ignored. Carbon. Per cent.	Combustion. Carbon. Per cent.
A4.....	$\begin{cases} 0.96 \\ 0.99 \\ 0.99 \end{cases}$	0.89	0.88
A6.....	$\begin{cases} 0.955 \\ 0.965 \end{cases}$	0.85	$\begin{cases} 0.85 \\ 0.85 \end{cases}$

LABORATORY OF HENRY DISSTON AND SON'S STEEL WORKS,
PHILADELPHIA, PA.

A BURETTE FOR ACCURATE GAS ANALYSIS.

BY ALFRED H. WHITE.

EVERYONE who has attempted to make accurate analyses of gases with the usual Hempel apparatus for technical gas analysis, knows there are many unavoidable sources of error, slight in themselves, but enough to make an exasperatingly large total at the end of a long analysis. The apparatus to be described was devised in the effort to eliminate some of these sources of inaccuracy. It is a modification of the Hempel burette with Petterson correction tube, the alterations being in the design of stop-cock and the position and form of the manometer, besides a change in the shape of the graduated tube to permit a more accurate reading of the gas volume. It has been used in its present form for the past year in this laboratory, and has been found to fulfil its purpose.

Some of the errors incident to analyses as usually conducted may be avoided by well-known precautions. If mercury instead of water is used as the liquid in the burette, errors due to solubility of the gas in the burette liquid and errors in reading due to water adhering to the walls of the burette, vanish. Errors due to solubility of gas in the reagent of the absorption pipette may be minimized by the use of a small quantity of the reagent in a pipette otherwise filled with mercury and may be greatly lessened when using an ordinary pipette by saturating the absorbing liquid with gas like that to be analyzed. Errors due to diffusion of gas through the liquid in the pipette are much more important than is usually believed, but may be obviated for most reagents by the use of a few cubic centimeters of mercury,

forming a trap at the bottom of the pipette. The errors which this paper aims to discuss and in part to remedy are those due to: Change in temperature and barometric pressure during an analysis; inclusion of air or leakage of gas while making connection with pipettes; and inaccuracy in reading gas volume.

Gas burettes in which the gas volume is unaffected by change of temperature and pressure have been devised and are well known. The Petterson correction tube as modified by Hempel, Drehschmidt, and others, consists of a glass tube of about the same dimensions as the burette, sealed at its lower end and with its upper end connected to one arm of a manometer whose other arm connects through a three-way stop-cock with the gas burette. This correction tube is enclosed in the same water-jacket as the burette, and hence the gas volume in it is affected by changes of temperature to just the same extent as the gas in the burette. When the liquid stands at the same height in both arms of the manometer, the pressure in the burette is the same as in the correction tube and therefore a constant, as the correction tube is sealed at its lower end. If the gas volume is read under these conditions it will be independent of changes in external temperature and pressure. There are several objections to the Hempel form of apparatus. The two rubber connections of the manometer may allow leakage of gas and consequent change in the supposedly constant pressure of the correction tube. Second, in drawing the gas out of the manometer into the burette there is a pronounced tendency on the part of the column of liquid to break when it starts down hill, especially at the rubber connection, with the result that some of it becomes carried into the burette with consequent change in the pressure indicated by the manometer. Figures 1 and 2 show the arrangement designed to overcome this difficulty. There is but one rubber connection in the manometer, and that is placed so that only mercury and never gas is brought in contact with it, thus rendering a leak with consequent change in pressure of the correction tube impossible. Communication with the manometer is established by turning stop-cock to position in Fig. 4. By placing the manometer below the stop-cock the further advantage is gained that in drawing the gas out of the manometer the mercury travels but a short distance and up hill only, meets with no bends
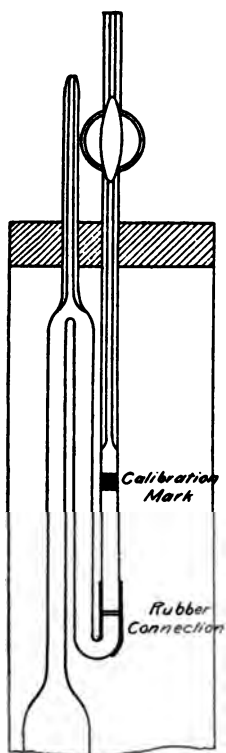
Fig. 1.
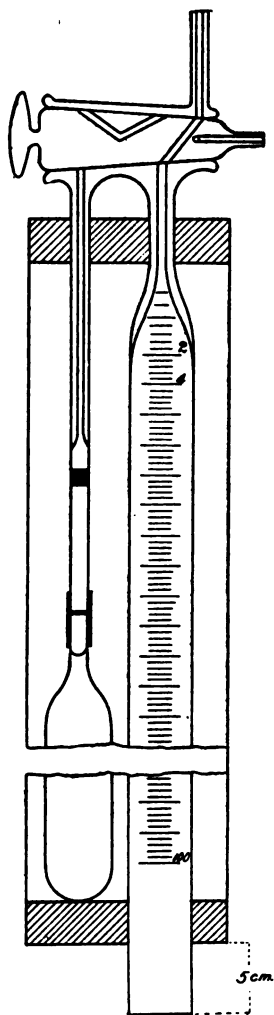
Fig. 2.
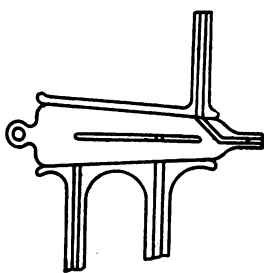
Fig. 3.
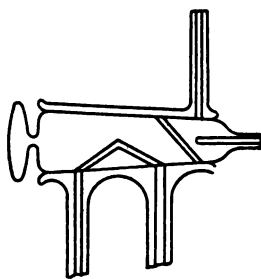
Fig. 4.

or inequalities in the tubing, and so may be drawn with great exactness to the stop-cock, drawing out all the gas without losing any of the mercury. The apparatus is all enclosed in the water-jacket and therefore all the same temperature, and is less cumbrous and apt to get broken than in other forms. The capillary tube projecting into the air behind the stop-cock as shown in Fig. 1 is to be sealed, under observed barometric pressure if desired, when the apparatus is first set up. The gas volume may be read when the mercury is at the same height in the two arms of the manometer and may then be reduced to standard conditions if desired. When this is not required, it is much more accurate to bring the mercury to a mark etched on the glass, or better tangent to the lower edge of a black metallic collar cemented around the manometer tube. In this case the gas will not be under the same pressure as that in the correction tube, but the variation will be a constant one and will cause no error. The connection between the burette and pipette is, as usual, made by a bent capillary tube and two rubber connections. Rubber connections, if properly made, introduce no appreciable error, but, because of their tendency to leak, form a serious menace to accuracy. Unfortunately no way has been found to dispense with them, and they are accepted by the author as a necessary evil. There is, however, an inherent source of error in the usual method of making the connection which the burette here presented completely obviates. With the apparatus ordinarily used, some of the gas under analysis will escape, or some unmeasured volume of air will be admitted to it whenever a connection is made. Perhaps usually both happen. The capillary tip of the burette, the connecting capillary, and the capillary tip of the absorption pipette, have a combined volume of about 0.5 cc. Although by various manipulative devices it is possible to restrict the error thus introduced from any individual operation to a fraction of this volume, it amounts in the course of a long analysis to a serious total. In the burette here presented it is completely eliminated.

By referring to Fig. 3, the stop-cock is shown turned in such a way that there is a clear passage from the capillary exit tube of the burette through the stop-cock to the outer air again. With the stop-cock in this position the pipette is to be connected

in the customary way to the burette but without any of the usual precautions to prevent inclusion of air. The liquid in the pipette is now blown up and through the capillary till it reaches the stop-cock. The capillary tube is thus completely filled with liquid. By turning the stop-cock to the position shown in Fig. 2 communication is established between the burette and pipette, and the gas may be passed over and absorbed as usual. After the absorption it is drawn over till the pipette-liquid just reaches the stop-cock, which is then turned back to the position in Fig. 3, allowing the liquid in the capillary of its own accord to siphon back into the pipette. The capillary is then to be rinsed out with a wash-bottle. In this way all the gas is each time drawn back into the burette for measurement. There is no gas lost in the capillary connecting tube, and no air is introduced, if the rubber connections have been properly made.

The gas volume in an ordinary gas burette may read with great accuracy with the assistance of a telescope, or some similar help, but it was desired to render such an adjunct unnecessary. The suggestion was taken from one of Bleier's[1] sketches. Fig. 5 shows schematically a gas burette with stop-cock and manometer as already described. The main body of the burette contains twelve bulbs, each of a capacity approximating 12 cc. A line is etched on each constriction and the capacity of the
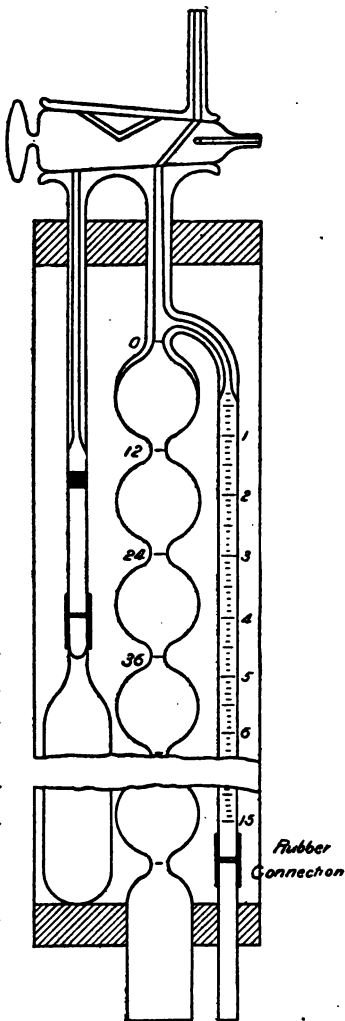
Fig. 5.

1 C. Bleier, "Ueber gasometrische Apparate." *Ber. d. chem. Ges.*, **31**, I, 238.

bulb between these marks is determined. Starting from the capillary above the top bulb a side arm springs, terminating in a small burette with total capacity of 15 cc. and graduated in 0.1 cc. Both these burette tubes connect at the bottom by means of heavy rubber tubes and a Y with a stop-cock on each arm, to a common leveling bottle. A screw clamp on each rubber tube serves for the exact adjustment of the mercury. To measure a gas, the stop-cock is placed in position in Fig. 3 and the mercury in the bulbed tube brought to the mark in one of the constricted portions by opening the proper stop-cock on the Y and raising or lowering the leveling bottle. When adjusted, the mercury is held in its proper position by closing the stop-cock on the Y. The stop-cock leading to the small burette tube is then opened and the gas brought to approximately atmospheric pressure by proper change in the mercury level. The three-way stop-cock at the top of the burette tube being now turned to position in Fig. 4, the burette is brought into connection with the manometer, which is properly set by further changing the level of the mercury in the small burette. The final adjustment in both burettes is made by the screw clamps on the rubber tubes. The volume of the gas will be read as x cc. in the bulbs $+ y$ cc. in side burette $+ z$ cc. in manometer. As there are these three readings to be made it is necessary that each be very accurate. Let us see how accurately this may be done. First, the mercury in the bulbed tube is to be brought to a specified mark in a tube of about 5 mm. internal diameter. By means of the screw clamp this may be done with such accuracy that the error is negligible. Second, the volume of gas in the side tube must be read. Each 0.1 cc. in this tube occupies a space of a little over 2.5 mm. and it is possible to interpolate 0.01 cc. with the eye with an error of less than 0.02 cc. Third, the mercury in the manometer must be brought to a definite mark with such exactness that the barometric pressure, under which the gas volume is read, shall be almost identical each time. A difference of 1 mm. of mercury pressure changes the gas volume 0.13 per cent., which on a volume of 100 cc. equals 0.13 cc., an error far too large. It was found impracticable to attain the required accuracy when it was attempted to bring the mercury to a mark etched on the glass. The best

device was found to be a band of thin, blackened copper, wrapped around the tube and cemented to the glass. It is possible to bring the mercury tangent to the lower surface of this with great exactness. In working with this burette the author is accustomed to make all readings in duplicate, readjusting at all points each time, and to repeat if the two differ from each other by more than 0.01 cc. Duplicates usually agree within this limit. The greatest difficulty found in manipulation is to draw the liquid from the pipette over exactly to the burette stop-cock and stop it there. If it gets into the burette, a bubble lodging in one of the capillary tubes frequently damps the sensitiveness of the manometer. If this happens the bubble may be shot out of its lodging place by compressing the rubber tube above the screw clamp. Such a bubble may also be carried into the manometer, where it will obscure the surface of the meniscus. To remedy this it is well to keep 2 or 3 mm. of water on the surface of the mercury in the manometer. This allows a perfectly sharp reading of the mercury meniscus below the water-level. The manometer should respond to a very slight movement of the screw clamp.

The advantages of this burette may be summarized as follows: It is a compact burette which, without reading-telescope or other accessories, allows the volume to be read with an error of less than 0.02 cc., compensates automatically for changes of temperature and pressure, and avoids completely all errors due to inclusion of air or loss of gas in making connections with the absorption pipettes. The disadvantages so far developed are chiefly those inherent in all forms of apparatus which possess a stop-cock and rubber connections. Both may leak; but on the other hand both may be kept so tight for limited periods of time as to introduce no measurable error.

Accurate apparatus is essential for accurate work and the author feels it but a just acknowledgment to thank Messrs. Greiner and Friedrichs for the care and skill with which they manufactured the burettes from his sketches.

ANN ARBOR, MICHIGAN,
April, 1900.

PREPARATION OF THE BLUE OXIDE OF MOLYBDENUM AND OF METALLIC MOLYBDENUM.

By ALLEN ROGERS AND F. H. MITCHELL.

BY the action of stannous chloride on an acid solution of a molybdate, a blue precipitate is produced. It was the investigation of this precipitate, that led to the following process : To prepare the blue precipitate, dissolve 50 grams of molybdenum trioxide in a sufficient quantity of ammonium hydroxide, to make a clear solution; to this add about the same quantity of water, make slightly acid with nitric acid, and then dilute with about five times its volume of water. To this solution add from 15 to 25 cc. of a 10 per cent. solution of stannous chloride. The very heavy precipitate which forms settles, and should be washed several times by siphoning off the supernatant liquid. These washings should be made as quickly as possible, as the blue precipitate becomes hydrated on standing, thus giving a deep blue solution.

After washing, the precipitate is thrown upon a plaited filter, and allowed to drain. It is then removed from the paper, while moist, into an evaporating dish, placed in the oven and dried at 100° C. This precipitate seems to correspond to the oxide of molybdenum, Mo_2O_3.

Place some of this oxide in a porcelain boat, and insert into an ignition tube, pass in hydrogen for a few minutes, then apply heat from a Bunsen burner for one hour, allow to cool, weigh and heat again for fifteen minutes; and continue heating until the weight is constant. The reduction takes from one hour to one and one-half hours, and may be hastened by moistening the oxide with a few drops of water. The molybdenum as prepared in this way is an ashen gray powder. The blue oxide is reduced more readily than the trioxide, under the same condition. In the electric furnace the blue oxide is rapidly reduced.

The accompanying figure illustrates a device by which we have been able to reduce various substances, and is very convenient in working with a small quantity.

The apparatus consists of a three-necked flask, A ; the carbons, B and B', are held in position by asbestos plugs. B' has a

cavity in the end, into which the substance to be reduced is inserted.   At C is an inlet and an outlet tube, by means of which an atmosphere of hydrogen is obtained.   Fill the cavity
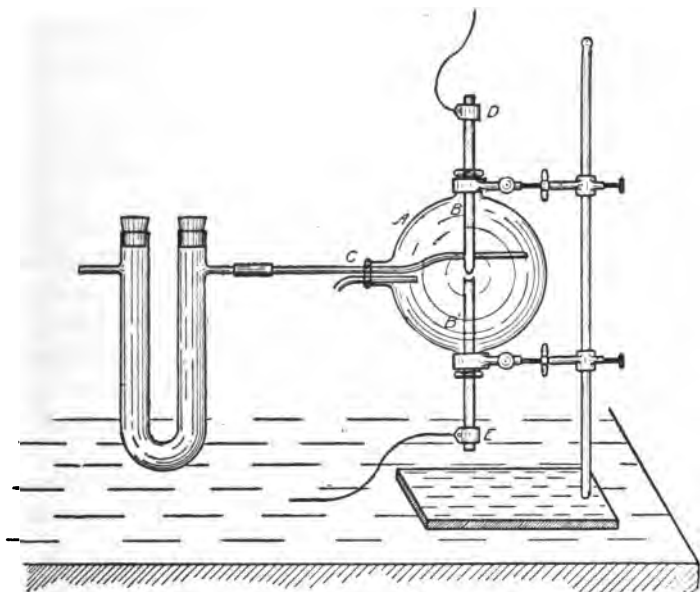
in B', remove the air, connect D and E with B and B', by means of copper foil, and having the proper resistance, turn on the current, and allow to pass until the desired effect is produced. The oxide was reduced in forty seconds, and, prepared in this way, resembles the product of the electric furnace; that is, a dull steel gray mass, which is very hard.

UNIVERSITY OF MAINE, ORONO, ME.

SOD OIL, WOOL GREASE, AND DEGRAS.

BY ERASTUS HOPKINS.

WHEN the tariff act of 1897, known as the Dingley bill, was made a law to govern the classification of imported articles, there appeared a paragraph in the act which, with an intent of definite designation, opened a question which became so involved that its final settlement was made only after litigation.

The paragraph is No. 279, which reads "....; wool grease, including that known commercially as degras or brown wool grease, one-half of one cent per pound."

The introduction of the term degras caused all the trouble, because the authorities framing the bill did not make the fact clear that the term degras is applied to oils and greases used by tanners without any special distinction.

For the question involved, research work was done in this laboratory on wool grease and sod oil, the results upon the latter being published in this Journal in 1899, p. 291.

As a result of the trial of the cases involved, sod oil was decided to be entitled to free entry as an oil, used expressly for currying leather not specially provided for in the act, paragraph 568, and not similar to wool grease. Since that time I have been so often approached by people regarding the facts pertaining to the substances involved in the case that I thought the subject might be of wider interest than to the limited circle of my professional acquaintances.

Sod oil and wool grease have entirely different constitutions as well as characteristics, and hence should be easily distinguished apart.

I wish especially to call attention to the terms "wool grease," "degras," and "sod oil."

Wool grease is extracted from the wool of sheep. Sod oil is expressed or extracted from leather which has been curried by oils, particularly fish oils.

Sod oil has no relation to wool grease in its derivation, but is related to it in its use; that is, for the currying of leather. Sod oil contains a resinous substance (not a resin) known as degras former, which is characteristic of sod oil. No other oil or grease (and this includes wool grease, which is, scientifically speaking, an animal wax and not a grease at all) contains this degras former, which is therefore characteristic of sod oil.

Originally, sod oil was called degras. Later the term was made by the American oil trade and to a less extent by the English to embrace wool grease. The term degras has therefore come to embrace two substances, dissimilar in constitution, source, and chemical constants. Wool grease being called degras by the trade, caused the mention of degras in paragraph 279 of

the act of 1897—a commercial term by which wool grease is known, as it is also known under the name of brown grease. The point I wish to make is that the degras there mentioned means wool grease but it does not embrace sod oil which in no way resembles it except in use. From this it can be seen that the term degras which originally had a limited meaning has come to be applied indiscriminately to the two substances used for currying and stuffing leather, and was mentioned in paragraph 279 to make that paragraph stronger in covering wool grease.

Paragraph 279 mentions two substances, tallow and wool grease. Degras is not mentioned in that paragraph excepting as a wool grease degras. Brown grease is mentioned also in this same connection.

Paragraph 568 mentions "all other greases and oils used for stuffing leather." Here also is included a degras but this degras is not that specially mentioned in paragraph 279 which is a wool grease, but is the original degras, or sod oil made from oil expressed from leather, and therefore having no connection with a wool grease which comes from wool. Sod oil is the English name for the substance known to the French as degras or moëllon and the term degras is the original French name for this oil extracted from oiled chamois leather and has been borrowed by the English to be misapplied to wool grease.

The term sod oil is unknown in the French currying trade excepting as an English translation of their own word degras or moëllon, and the process of making degras might be said to have originated in France in the manufacture of chamois leather.

(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.)

A METHOD FOR THE DETERMINATION OF ZINC BY THE USE OF STANDARD THIOSULPHATE SOLUTION.[1]

BY RICHARD K. MEADE.
Received May 4, 1900.

A T the spring meeting of the Lehigh Valley Section, the author read a paper[2] upon a new volumetric method for magnesium. The method depended upon the precipitation of

1 Read at a meeting of the Lehigh Valley Section, January 18, 1900.
2 This Journal, 21, 746.

the magnesium as magnesium ammonium arsenate, $Mg_2(NH_4)_2$-$As_2O_8+H_2O$, and the determination of the arsenic in this precipitate by digestion with potassium iodide in a strongly acid solution, and titration of the liberated iodine with standard thiosulphate. When a solution of arsenic acid contains sufficient sulphuric or hydrochloric acid, the arsenic is quickly reduced by potassium iodide even in the cold from the higher to the lower state of oxidation. The reaction is expressed by the equation

$$As_2O_5 + 4KI + 4HCl = As_2O_3 + 4HCl + 2H_2O + 2I_2.$$

Zinc is usually determined as a pyrophosphate by precipitation as zinc ammonium phosphate and ignition of this latter. Since the method above outlined for magnesium was suggested by the analogy between the phosphates and arsenates, the thought also occurred to me to make use of a volumetric method for determining zinc, somewhat similar to that for magnesium, by precipitating the zinc as an arsenate instead of a phosphate and determining the arsenic in the precipitate by titration with standard thiosulphate solution. From the equation given above and the formula for the zinc ammonium arsenate, each cubic centimeter of decinormal sodium thiosulphate should be equivalent to 0.00327 gram of zinc.

The method as tried for zinc was as follows : Pure zinc oxide, ZnO, was dissolved in dilute hydrochloric acid, an excess of ammonia added, and then 50 cc. of a 10 per cent. solution of sodium arsenate. The solution, after dilution to about 750 cc., was next warmed and nitric acid added until a slight turbidity was produced when the addition of nitric acid was discontinued and acetic acid added in its place, 1 cc. at a time, until the solution reacted acid to test paper. The precipitate was changed from curdy and flocculent to heavy and granular by heating and stirring. After allowing the precipitate to settle it was filtered off and washed. A hole was next punctured in the filter-paper, the zinc ammonium arsenate washed into a beaker, and 50 to 60 cc. of dilute hydrochloric acid added. The paper and the beaker in which the precipitate was formed were washed with the dilute acid until the solution and washings measured 85 to 100 cc. when from 2 to 3 grams of potassium iodide were added to the solution, and after allowing this latter to stand in

the cold a few minutes, the standard thiosulphate was run in from a burette until the color of the solution faded from red-brown to pale straw color and then, drop by drop, until all color vanished. The addition of starch for an indicator of the end of the reaction was found unnecessary in both the determination of magnesium and zinc by this method. Below are the results:

	Zinc oxide taken. Gram.	Equivalent in Zinc. Gram.	Zinc found. Gram.
1...............	0.2490	0.2000	0.1998
2...............	0.2490	0.2000	0.1994 ·
3...............	0.2490	0.2000	0.2002
4...............	0.1245	0.1000	0.1004
5...............	0.1245	0.1000	0.1002
6...............	0.1245	0.1000	0.0998

Since calcium and magnesium are precipitated from alkaline solutions by sodium arsenate while zinc from an acid one, the successful attempt was made to separate the latter from the former two by first making the solution strongly ammoniacal, adding sodium arsenate, filtering off the calcium and magnesium arsenates, then making the solution acid with nitric and acetic acids and filtering off and determining the zinc as described above. The completeness of the separation is shown by these results.

Zinc oxide taken. Gram.	Equivalent in zinc. Gram.	Calcium carbonate added. Gram.	Magnesium oxide added. Gram.	Zinc oxide found. Gram.
0.2490	0.2000	0.2000	0.1000	0.1996
0.2490	0.2000	0.2000	0.1000	0.1992
0.2490	0.2000	0.2000	0.1000	0.2004
0.0623	0.0500	0.2000	0.2000	0.0500
0.0623	0.0500	0.2000	0.2000	0.0502
0.0623	0.0500	0.2000	0.2000	0.0496

Unfortunately manganese can not be so easily separated from zinc. In the case of ores, etc., it may, however, readily be gotten rid of by treatment with potassium chlorate and nitric acid after the solution of the ore.

The determination of zinc in a sample of ore was tried by first throwing down the manganese as a dioxide with potassium chlorate and nitric acid and filtering, separating the iron and alumina by double ammonia precipitations, then adding a large excess of sodium arsenate and filtering off the calcium and magnesium arsenates formed, and finally precipitating the zinc

by addition of nitric and acetic acids. The iodine liberated by digesting this precipitate in an acid solution of potassium iodide was then titrated with standard thiosulphate and the zinc calculated from the reading on the burette. The time required to run four determinations, without any effort at speed, was about eight hours.

The analysis of the ore by careful gravimetric methods was

	Per cent.
Zinc oxide	37.58
Manganese monoxide	15.33
Ferric oxide	29.69
Calcium oxide	1.12
Magnesium oxide	0.77
Silicon dioxide	12.77
Carbon dioxide	1.23
Water	0.76
	99.25

Metallic zinc, 30.18 per cent.

By the volumetric method, outlined above, the results were

	Metallic zinc. Per cent.
1	30.00
2	29.98
3	30.04
4	29.98

LAFAYETTE COLLEGE, EASTON, PA.,
January 18, 1900.

NOTES.

The Alleged Adulteration of Milk with Brain-matter:[1]— In the 1898 report of the Dairy Commissioner of the State of New Jersey, page 50, one of the chemists acting for the Commissioner, refers in rather intemperate language to the statements made in some text-books, concerning brain-pulp as a possible adulteration of milk and asserts that such adulteration has never occurred. He quotes the statement of König[2] to the effect that such addition to milk involves practical knowledge and resources which would hardly be possessed by milk-producers or purveyors, but Dr. König has not foreseen

[1] Read before the Philadelphia Section of the American Chemical Society, March 15, 1900.

[2] *Nahrungs- u. Genussmittel*, 2, 256.

the spread of education and the aid that such people may get from books and even from newspapers. We may, however, judge from König's statement that the German reports give no authentic instance of such addition, but we would be mistaken if we were to regard the allegation as on the same par with the popular fallacies about sand in sugar or chalk and water as a milk substitute. A consultation of trustworthy authorities will furnish some interesting data.

The earliest reference to the subject seems to have been in an anonymous article in the *Gazette d. Hôpitaux* (1841). Unfortunately the file of the *Gazette* at the College of Physicians lacks the numbers for 1841, but the general opinion of those who have consulted the article is that its statements are not worthy of credit. It appears to have been written in consequence of the agitation in France at that time over the enactment of laws regulating the sale of milk. The general subject of the composition of milk, its adulterations and the means of detecting them, had been discussed at great length by Quevenne in the *Ann. d. Hyg. Pub. et d. Med. Leg.* for 1841. In the same journal for 1842, many pages are given to the discussion of the adulteration of milk by brain-matter, the papers being by Quevenne and Gaultier de Claubry. A summary of the paper by the latter author is published in the *Bull. d. Acad. d. Med.*, 7 (1842). Quevenne regards the adulteration as unlikely, and thinks that it could not serve as a means of concealing added water but might be made to conceal skimming.

These French experimenters found that milk that had been adulterated by them with brain-matter presented properties different from those described by the anonymous writer in the *Gazette*.

A. H. Hassell, in his work on "Food Adulteration" (1876, p. 418) states that Mr. Queckett, the famous microscopist, exhibited drawings made from examinations of milk containing nerve tissue. It is further on record that Queckett stated before a committee of the House of Commons that he had found such structures in the sediment from a sample of milk examined about 1850, but had not observed it since. He submitted drawings of fields obtained from cows' milk with and without addition of calves' brains. As Queckett was an accomplished microscopist

and a scientific investigator, it does not seem likely that he would be mistaken on this point and he was evidently sure enough of it to make drawings of what he saw, and bring them to professional and official notice. We may, therefore, accept this record as one of trustworthy character. Hassell figures, on page 426 of the work above noted, a field showing the appearance of milk containing brain-matter, but does not state whether it is a copy of Queckett's drawings or from a sample prepared for the purpose.

Additional evidence as to this form of adulteration is presented in a communication by Sidney Gibbons, F. C. S., in the *Chemical News*, 33, 134 (1874). After a brief reference to the statements of Hassell and Queckett, Mr. Gibbons details an interesting experience of which the following is an abstract:

At a suburban hotel, near Melbourne, Victoria, frequent complaints had been made of the quality of the milk supplied, and on a certain date a sample was furnished to the chemist. As received, the sample had formed into three layers, the highest and lowest being thick and dirty gray, the middle one thin and colorless. When shaken, the mass became uniform and pulpy without frothing but stratified again on standing. Its specific gravity was 1022. The top layer did not closely resemble cream and contained but few fat-cells. The lowest stratum was darker, including dirt, sand, and vegetable matter. Much granular and clotted matter was present which was distinguished from fat by staining with magenta. There was no material amount of starch, though a few granules were present. Many peculiar cell-structures resembling brain-cells were seen under the microscope. Mr. Gibbons mixed some sheep's brain with milk and obtained optical appearances similar to those in the sample. He did not succeed, however, in making so smooth a mixture, possibly because the milkman had manipulated the material more elaborately. The fields observed agreed closely with the drawings given by Hassell.

From these reports it seems justifiable to record brain-matter, especially calves' and sheep's brains, as adulterations of milk that have occurred and may again occur, and therefore not to be overlooked in the analytic manuals.

Quevenne and Gibbons incline to the view that this form of adulteration is not dangerous to the public health, although, of course, not in any sense permissible. Such views may be easily excused when we consider how little was known, even at the date of Gibbons' report, concerning the diseases likely to be conveyed by milk. The view of the French and English chemists is based on the fact that brain-matter is a regular article of food but this loses its value when we remember that for such purpose the brains are cooked, which would be rarely the case when used for milk adulteration. Apart from the liability of the brain to contain virulent microbes, the localization there of certain stages of dangerous entozoa is by no means infrequent.

It is a question whether some of the special milk-laws would cover this form of adulteration but it is clearly prohibited by the general food-law in operation in most of the states of the United States, and butter made from such milk would come under the provisions of the national and state laws concerning oleomargarin.

It seems to me that this form of adulteration might easily escape notice. Brain-matter may give a rich creamy color to skimmed milk. All those who have written about the subject have spoken of the use of the microscope for detecting the adulterations, but in the routine inspection of milk-supplies, microscopic examination is rarely employed, and hence the adulteration might be overlooked. I have prepared samples by adding to skimmed milk, some calves' brain well pulped and strained through a close-mesh sieve. The nerve tissue can easily be seen with a moderate magnifying power. Evaporation in a milk-dish does not show anything different from ordinary milk, but the odor emitted when the residue is charred, preparatory to taking the ash, is suggestive of foreign animal matter. When the sample was treated with the mixture of pentyl-alcohol and hydrochloric acid, and then with strong sulphuric acid in the usual manner for rapid fat-determination, no peculiar reactions were noted. The proteids dissolved quite as readily in the acid as that from pure milk. The brain-pulp was found to be rapidly soluble without striking color in cold strong sulphuric acid.

HENRY LEFFMANN

A New Form of Receiver for Fractional Distillation in Vacuo.[1] —
While there are several forms of receivers which give sat-
isfaction, when small quantities of liquids are fractionated
in vacuo, most of them are open to the serious objection that
it is necessary to destroy the vacuum to change receivers or to
remove all or part of the distillate; these difficulties are entirely
obviated by the apparatus shown in the figure.

The receiver consists of three separatory funnels sealed
together, each of the three bulbs being provided with a side stop-
cock, the uppermost having an additional one, which is con-
nected with the vacuum pump.

The condenser tube enters into the top bulb, connection being
made by a ground glass joint, for which a rubber stopper may be
substituted if desired.

The *modus operandi* is obvious and almost automatic; the stop-
cocks *a, d, e,* and *f* are closed, *b, c,* and *g* opened, the last being
connected with the vacuum pump; the first fraction is collected
in bulb A, the stop-cock *b* closed, and the second fraction col-
lected in bulb B; by closing stop-cock *c,* the third fraction may
be collected in bulb C.

If it is desirable to separate the distillate into more than three
fractions, or if the quantity of the distillate exceeds the capacity
of the bulbs (which may be 1 liter each), the apparatus shows
its special advantages.

Suppose the first fraction has been collected in bulb A and the
second is being received in B; by opening stop-cock *d,* air is ad-
mitted into A, and the contents withdrawn through *a;* closing
this and connecting *d* with a second pump, the vacuum is re-
established in A. This point may be ascertained without the
aid of a separate manometer by slightly opening *b* when, if the
vacuum is less in A than in B, air will bubble through the liquid
in the latter, while if the pressure in both bulbs is the same, or
if it is less in A, the distillate will flow down to A, where it
may be collected and drawn off as before, and the operation
repeated *ad infinitum.*

With a little experience a receiver of a total capacity of
three liters may be so manipulated as to distil several liters of
liquid without interruption. In actual practice 40 liters are

regularly distilled in this way, and each fraction is made sharp
and exact, as there is no disturb-
ance of the vacuum.

With bulbs of smaller capacity,
e. g., 250 cc. each, it is unnecessary
to employ more than one pump,
since the vacuum will not appre-
ciably diminish in the short time
necessary to close *g*, disconnect
the pump, attach it to *d*, and rees-
tablish the vacuum in this bulb.
A makeshift apparatus, embodying
the principles of the one shown in
the sketch, can be made in any
well-equipped laboratory by con-
necting three separatory funnels
by means of two-holed rubber
stoppers, the other holes being oc-
cupied by bent glass tubes provi-
ded with stop-cocks or even rubber
tubing and pinch-cocks.

For continued use the apparatus
with the bulbs sealed together is to
be recommended; the one described
has been used almost daily by the
writer and was made according to his designs by E. Greiner,
No. 62 Centre Street, New York.
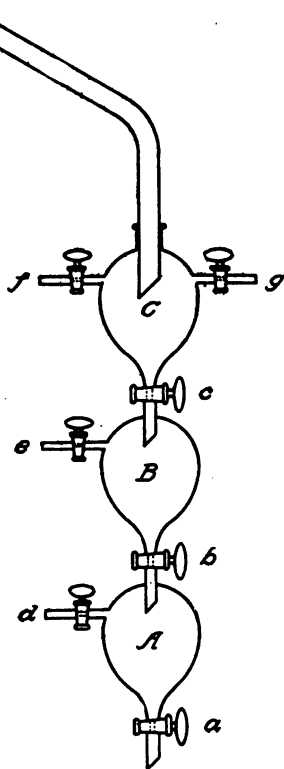
LUCIEN FOGETTI.

OBITUARY.

Hon. Nathaniel Peter Hill, of Denver, Colorado, scientific
metallurgist, sometime professor of chemistry in Brown Univer-
sity, and later United States Senator from Colorado, was born
in Montgomery, N. Y., February 18, 1832; he died in Denver,
Colorado, May 22, 1900.

His father and mother were notable people in Orange County,
N. Y. The father, a well-to-do and substantial farmer, had
been lieutenant of cavalry in the war of 1812 and subsequently
he held many offices of trust in his county where he was

respected as a man of superior abilities and high character.

When Senator Hill entered Brown University in the year 1853 he was a bright and promising young man, matured and developed by the responsibility which had come upon him, while yet little more than a boy, of managing the farm after his father's death. His interest in scientific agriculture led him to devote his chief attention to chemistry, and his progress in the subject was so rapid and so substantial that he was soon made an instructor, and in 1859, he was appointed professor of chemistry. He soon set about the securing of funds for a new chemical laboratory for the university, and he accomplished the work of its construction in 1862.

A little later his attention was directed to the freshly opened gold-bearing districts in Colorado. The field appeared so promising that in 1864 he resigned his professor's chair and turned his attention to practical metallurgy. He was early impressed with the necessity of *smelting* rather than *milling* the Colorado ores of Gilpin County, and he proceeded to make a careful study of the whole subject at the metallurgical works of Freiberg, in Saxony, and Swansea, in Wales. As a result; he formed a business connection with the noted house of Vivian & Sons in Swansea. In 1867 he organized the Boston and Colorado Smelting Co., a concern which has operated successfully for over 30 years and of which up to the time of his death he was the general manager. Professor Hill is acknowledged as the chief agent in the creation of that great industry which was necessary to the development of the mineral resources of his adopted State.

Space does not permit a full statement here of his achievements, but a partial enumeration of his official and business positions speaks volumes. He was mayor of Black Hawk, Colorado, in 1871; member of the Colorado Territorial Council, 1872–3; United States Senator from Colorado, 1879–1885; member of the International Monetary Commission, 1891; president of the United Oil Company, working in the Florence district; president of the Colorado Smelting and Mining Company, operating on an extensive scale in Montana; president of the Denargo Land

Company, engaged in developing real estate in the vicinity of Denver; principal owner of the *Denver Republican*. .

As a chemist and scientific man Professor Hill was characterized by clear insight, great grasp of his subject, and sound judgment. His scientific work related chiefly to applied chemistry. During his professorship in Brown University he continually acted as expert and adviser in connection with chemical manufacturing establishments in and near Providence. But his life-work was in metallurgy, and the complex operations of his refining establishments near Denver are a monument to his power in the scientific treatment of metallic ores. As a university professor he was highly valued; he was not only recognized as a master of his subject and as a clear thinker, but more, he was loved by his pupils as a true gentleman. He was a remarkably able business man, having far-sightedness, wisdom, and courage. As a legislator he secured—as he merited it—a reputation for ability, dignity, and integrity.

Professor Hill married Miss Alice Hale, of Providence, R. I., a member of a remarkably able New England family, and a woman of superior powers and great sweetness of character. She survives him with three children: Crawford Hill (A. B., Brown University, 1885), Miss Isabel Hill, and Mrs. Gertrude (Hill) Berger. J. H. APPLETON.

NEW BOOKS.

ANALYSE ÉLECTROCHIMIQUE. PAR EDGAR F. SMITH, Professeur de Chimie a l'Université de Pennsylvanie. Traduction par Joseph Rosset, Ingénieur civil des Mines. Paris: Gauthier-Villars. 1900.

The hearty favor with which this excellent little work was received on its first appearance by English-speaking chemists, and its translation into the two languages that can boast of more voluminous electrochemical literatures than the English, are doubtless sources of much gratification to its author. This French version, like the German that preceded it, is a clear and faithful translation of the second American edition of 1894. It contains a few changes and additions such as the separation of some of the platinum metals, analytical results, and some useful tables, yet these are hardly of sufficient importance to justify the

translator's claim "c'est donc en quelque sorte une édition origi-
nale paraissant en français que nous présentons." As a fea-
ture quite unusual in French books of this kind, we note that
careful attention has been given to the spelling of the names of
foreign authors. H. F. KELLER.

ERRATUM.

On page 139, line 10, of February, 1900, issue, for the formula
"$[(CH_3)_2NH]_2TeCl_6$" substitute "$[(CH_3)_2NH]_2TeCl_6$."

Proceedings.

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ADDRESS WANTED.

Schoen, Joseph, formerly of 3602 Lake Ave., Chicago, Ill.
Wood, J. R., formerly of 439-441 Green St., Philadelphia, Pa.

MEETINGS OF THE SECTIONS.

WASHINGTON SECTION.

The regular meeting was held October 12, 1899.

The first paper was read by Mr. J. K. Haywood and was entitled "The Determination of Glycogen," by J. K. Haywood and W. D. Bigelow.

The authors proved that methods for the estimation of glycogen, which depend on its direct inversion into dextrose, are unreliable and have modified the method of Brücke so as to make it accurate and fairly rapid.

The second paper was read by Dr. F. K. Cameron and was entitled "A Method for Estimating Black Alkali in Soils."

The method enables the determination of the degree of hydrolization of the sodium carbonate in soils and soil crusts containing this compound. It was shown that an accurate determination of the amount of sodium carbonate could not be made by titrating directly with a standard acid, two reactions taking place with the formation of the acid carbonate in varying quantities and furthermore the probable existence of acid carbonate in the soil adds to the difficulty of such a determination. It was shown that acid potassium sulphate is free from these objections, the reaction taking place with quantitative exactness according to this equation :

$$Na_2CO_3 + HKSO_4 = NaHCO_3 + NaKSO_4$$
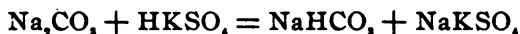
both substances indicated in the right-hand member of the equation being natural. It should be borne in mind that acid sodium carbonate although a neutral substance towards indicators, quite rapidly and readily inverts with the formation of the alkaline normal carbonate, so that a reasonable degree of speed must be used in making the titrations.

Details of the practical application of the method with examples from practice, were given, and it was shown that in ordinary practice the method was easily capable of an accuracy indicated by a probable error of less than 0.02 per cent.

The last paper was read by Dr. H. W. Wiley, and was entitled "The Fifteenth Annual Meeting of the Association of Official Agricultural Chemists, at San Francisco, July 5–7, 1899."

Mr. Tassin exhibited a specimen of calcium chloride which he

had obtained from a muck soil found in Utah. The salt occurs as an incrustation between Salt Lake City and Salt Lake.

Dr. Bolton exhibited a bibliography of thallium compiled by Miss Martha Dunn and recently published by the Smithsonian Institute. He called attention to the work done in Paris by Jules Garcon, who has published a bibliography of the " Chemical Technology of Textile Fibers," and a pamphlet entitled " Resources of Bibliography of Chemistry." The latter consists of a list of chemical bibliographies.

The regular meeting was held on November 9, 1899.

The first paper of the evening was read by Dr. H. Carrington Bolton and was entitled " Reminiscences of Bunsen and the Heidelberg Laboratory, 1863-65."

The speaker related anecdotes of Bunsen, and events that occurred in the Heidelberg Laboratory during the third semester which he spent there. Contemporary with him were the following Americans :

Eli W. Blake, afterwards professor of physics, Brown University, deceased ; Owen W. Root, afterwards professor of chemistry, at Hamilton College, N. Y., deceased ; Charles Wolf, of Cincinnati, deceased ; Frank Slingluff, of Baltimore ; Harry McBurney, of Boston ; Lyman Nichols, of Boston; Arnold Hague, of the U. S. Geological Survey.

The second paper of the evening was read by Dr. H. Carrington Bolton and was entitled " Chapters on the History of the Thermometer ; I.—The Open Air Thermoscope of Galileo."

The primitive form of the thermometer was invented about the year 1595 by Galileo ; this is proved by extant letters addressed to him by his pupil and friend Sagredo. The instrument was an open air thermoscope of the inverted type, and was early applied to meteorological observations, to testing the temperature of fever patients, and to noting temperature of freezing-mixtures.

The very common statement that the thermometer was the invention of C. Drebbel, of Holland, has no basis of fact, as shown by his own publications, copies of which were exhibited by the speaker.

The third paper was read by Dr. F. W. Clarke and was entitled "The Action of Ammonium Chloride upon Certain Silicates," by F. W. Clarke and George Steiger.

The authors described a series of experiments in which various silicates were heated in a sealed tube to 350° C. with dry ammonium chloride. After leaching out the contents of the tube with water it was found that alkalies were removed as chlorides and replaced by ammonia. Analcite and leucite are thus transformed into an ammonium leucite:

$$NH_4Al.Si_2O_6,$$

which is perfectly stable at 300° and only begins to decompose when heated in the open air to 350°.

Some eight other silicates were given preliminary study and the reaction was found to be fairly general. The product from natrolite contained 8.3 per cent. of ammonia and other zeolites took up from 4 to 6 per cent. The investigations are to be continued.

The fourth paper was read by Dr. F. K. Cameron and was entitled "Hydrochloric Acid and Aqueous Phenol," by F. K. Cameron and J. A. Emory.

The authors determined the freezing-point curve for hydrochloric acid solutions, saturated with respect to phenol. Each independently determined the concentrations of the various solutions and their freezing-points for intercomparison. The curve was found to be a straight line, parallel to the curve for water and hydrochloric acid alone, from which it would seem that the solubility of phenol is practically constant through the range of temperature involved, and the lowering of the freezing-point of the solvent is a purely additive effect of the two solutes.

The fifth paper was read by Dr. F. K. Cameron and was entitled "The System Water, Hydrochloric Acid, and Phenol," by F. K. Cameron and W. H. Krug.

On lowering the temperature of the system, solid phenol separates. But if the initial mass of water be relatively large its concentration with respect to hydrochloric acid is practically unaffected while the solid phenol is separating and consequently the temperature of the phenol remains very constant. The freezing-point curve for phenol in contact with aqueous solutions of

hydrochloric acid of various concentrations, was determined. Its practical value for a rapid determination of the approximate strength of hydrochloric acid solutions was indicated.

<div align="right">WILLIAM H. KRUG, *Secretary*.</div>

CHICAGO SECTION.

The November meeting of the Chicago Section was held at the Technical Club, November 24, 1899.

After the usual dinner, Prof. Julius Stieglitz, of the University of Chicago, gave a very interesting paper on the "Theory of Ionization in Analytical Chemistry."

He showed the value of the theory in explaining analytical reactions, thus adding to the scientific side of purely analytical chemistry. His remarks were illustrated with many experiments.

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The thirty-first meeting of the Chicago Section was held at the Technical Club, December 13, 1899.

The following program was presented :

"An Apparatus for the Distillation of Ammonia with Steam," by Edward Gudeman.

"Notes on the Determination of Arsenic in Antimonial Lead," by Gustav Thurnauer.

"On the Action of Acyl Chlorides on the Disubstituted Ureas," by F. B. Dains.

These officers were elected for the year 1900 : *President*, W. R. Smith ; *Vice-President*, Geo. H. Ellis ; *Treasurer*, C. W. Patterson ; *Secretary*, F. B. Dains ; *Executive Committee*, The President, the Secretary, Wm. Hoskins ; *Member of the Council*, E. Gudeman.

<div align="right">F. B. DAINS, *Secretary*.</div>

NORTH EASTERN SECTION.

The regular monthly meeting of the section was held in Boston on Wednesday evening, November 22. President A. D. Little called the meeting to order, 68 members being present. After the secretary's minutes were read and approved, the election of three members to represent the section in the council was held. The members elected were H. P. Talbot, L. P. Kinnicutt, and T. W. Richards.

Fred. L. Dunlap, of Worcester, presented a paper on "Cata-

lytic Action, with Special Reference to Its Application to the Manufacture of Sulphuric Acid." The second paper was by Walter L. Jennings, of Worcester, on "The Constitution of Rosaniline Dye Stuffs." At 10.30 the meeting adjourned.

The December meeting of the section was held in Boston on December 16, President Little in the chair, and 52 members present. After transacting the regular business of the section, Mr. A. D. Little presented a paper on "Viscose (cellulose sulphocarbonate) and Its Applications."

Mr. Little gave a review of the chemistry of cellulose, explained the method of preparation of viscose, and described some of its many applications, illustrating the paper by experiments and samples. After a discussion of the paper the section adjourned.
                                    W. H. WALKER, *Secretary.*

Proceedings.

MINUTES OF THE TWENTIETH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The meeting was called to order at 9.15 A.M., Wednesday, December 27, 1899, in the Kent Chemical Laboratory, Yale University, New Haven, Conn., with President Edward W. Morley in the chair. Professor S. W. Johnson, of Yale University, was introduced and in a brief address extended a cordial welcome to the visiting chemists. President Morley responded in behalf of the Society.

The minutes of the previous meeting were approved as recorded in the secretary's book.

Papers were then read and discussed as follows: "The Action of Ammonium Chloride upon Certain Silicates," by F. W. Clarke and George Steiger; read by Professor Clarke. The paper was discussed by Messrs. Johnson and Clarke.

"The Specific Gravity of Copperas Solutions Containing Free Sulphuric Acid," by Edward Hart.

"The Allotropic Forms of Selenium," by A. P. Saunders. Discussed by Messrs. Dennis and Saunders.

"Synthesis of 2-3,3-Trimethylcyclopentanone," by W. A. Noyes ; read by Edgar F. Smith.

"The Action of Unsymmetrical Phenyl-hydrazines on Chlorquinones," by Wm. McPherson ; discussed by Messrs. Bogert, McPherson, and Freer.

A motion to appoint a representative from the American Chemical Society to act together with representatives from other organizations, in case it should be found desirable, to constitute a committee to consider the claims of chemistry in courses of education was, upon motion of Professor Atwater, referred to the council with power.

A paper by L. P. Kinnicutt and George R. Sanford on "The Iodometric Determination of Small Quantities of Carbon Monoxide," was read by Dr. Kinnicutt.

W. O. Atwater then presented a paper on "The Conservation of Energy in the Living Organism," and in connection with the paper explained the respiration calorimeter used in investigations upon the subject at Wesleyan University, Middletown, Conn.

After some announcements the morning session was adjourned.

WEDNESDAY AFTERNOON, DECEMBER 27, 1899.

A visit was made to Middletown, under the leadership of Professor W. O. Atwater, for the purpose of inspecting the laboratories and buildings of Wesleyan University, and witnessing the method of conducting investigations with the respiration calorimeter.

Before returning to New Haven, the visiting chemists enjoyed the hospitality of Professor Atwater and his family at his home where light refreshments were served.

WEDNESDAY EVENING, DECEMBER 27, 1899.

The address of the retiring president, Edward W. Morley, was delivered in Osborn Hall, at 8 P.M.: Subject, " Are New Processes Needed for the Determination of the Atomic Weight of Oxygen?"

After the president's address the chemists enjoyed a "smoker" at the New Tontine Hotel where Professor Wm. H. Brewer entertained them with some reminiscences of old chemists.

THURSDAY MORNING, DECEMBER 28, 1899.

The session was called to order in the Sheffield Chemical Laboratory, at 9.15 A.M. The reports of the secretary and the editor were read and ordered placed on file, as was also the report of the Committee on Papers and Publications.

The reports of the acting librarian and of the Finance Committee were read and referred to the Council. F. W. Clarke then presented the report of the Standing Committee on Atomic Weights and the report of the International Committee on Atomic Weights. The former was referred to the Committee on Papers and Publications and, on motion of Dr. McMurtrie, the report of the International Committee on Atomic Weights

was adopted, the president was authorized to appoint the necessary committee, and the other officers were empowered to carry out the recommendations of the report.

The report of the treasurer was read and placed on file

A communication was received from E. E. Ewell, chairman of the Committee on Standards for Instruments of Measure, in which certain resolutions were presented to the Society. On motion of Dr. Talbot the communication and resolutions were referred to the Committee on Standards for Instruments of Measure for consideration and report to the council of the Society, which was requested to take action in the matter, and the Committee on Standards for Instruments of Measure was empowered to increase its number for the purpose of considering this subject.

Dr. McMurtrie made an announcement regarding the Fourth International Congress of Applied Chemistry which is to be held in Paris during the coming summer.

The results of the balloting, in the annual election for councilors and president, were announced by President Morley as follows : Councilors at large, elected to serve for three years, beginning January 1, 1900, F. W. Clarke, F. P. Venable, Chas. F. Mabery, and S. P. Sadtler; President of the Society for the year 1900, Wm. McMurtrie. Dr. McMurtrie, the president-elect, was then introduced by President Morley and made a few remarks in appreciation of the honor conferred upon him.

The following papers were presented : '' A Demonstration of the Properties of the Isomeric Form of Potassium Ferricyanide,'' by James Locke; '' Bacterial Treatment of Sewage in England,'' by L. P. Kinnicutt; '' Preparation of Samples for Analysis,'' by S. W. Johnson; '' What is Plant Food ? '' by H. W. Wiley.

The report of the Committee on Patent and Related Legislation was received and placed on file.

On motion of H. W. Wiley, the thanks of the Society were extended to :

The faculty and corporation of Yale University, the officers in charge of the Connecticut Agricultural Experiment Station, the Local Committee of Arrangements for the Meeting, Professor Wm. H. Brewer, Professor W. O. Atwater, the New Haven Colony Historical Society, the governors of the Graduates' Club,

the citizens of New Haven, and the trustees of the Chemists' Club of New York, for hospitalities and courtesies shown to the visiting chemists and for their untiring and successful efforts to make the Twentieth General Meeting of the American Chemical Society a most enjoyable and memorable occasion.

The Society then adjourned to meet at the New Tontine Hotel at 7 P.M.

THURSDAY AFTERNOON, DECEMBER 28, 1899.

The council met in the Kent Chemical Laboratory at 2 P.M.

The afternoon was spent by the other members of the Society in visiting the buildings, laboratories, and collections of Yale University, etc.

THURSDAY EVENING, DECEMBER 28, 1899.

The members of the Society enjoyed a subscription dinner at the New Tontine Hotel. The retiring president, Edward W. Morley, presided and H. W. Wiley acted as toast-master.

Toasts were responded to as follows:

" The Retiring President"—Edward W. Morley. "The Incoming President"—Wm. McMurtrie. " Agricultural Chemists "—S. W. Johnson. " Old Bachelorhood"—Chas. B. Dudley. "Lady Members of the Society"—Charlotte A. Bragg. "The New York Section "—Chas. F. McKenna. "The Rhode Island Section "—E. D. Pearce. " The Northeastern Section "—L. P. Kinnicutt. " The Washington Section "—H. N. Stokes. " The Philadelphia Section "—Edgar F. Smith. " The Michigan Section"—Paul C. Freer. "The Lehigh Valley Section" —Edward Hart. "The Local Committee "—H. L. Wells.

The Twentieth General Meeting of the American Chemical Society then adjourned *sine die.*

ALBERT C. HALE, *Secretary.*

ANNUAL REPORT OF THE SECRETARY OF THE AMERICAN CHEMICAL SOCIETY, DECEMBER 26, 1899.

The past year of the Society has been one of continued progress and development. The membership has increased from 1415 to 1569; two new sections have been formed, one in Philadelphia, the other in Michigan with headquarters at Ann Arbor; a fund has been permanently invested to cover all

amounts that have ever been received for life membership;
several committees have completed their work and have been
discharged, and to new committees new work has been assigned;
the Journal has been filled with valuable papers, and the demand
upon its columns has been so great that its regular issue has
been enlarged to 100 pages, and for the last three numbers a
special edition of 150 pages has been authorized in order to make
room for material that had accumulated in the hands of the
Committee on Papers and Publications. The papers that have
appeared in the Journal have been quite fully abstracted by other
scientific periodicals both at home and abroad, and some of them
have been reproduced entire. The address of the retiring presi-
dent of the Society last year, Professor Charles E. Munroe,
appeared in the journal *Science*, and the information therein
contained was considered of such value that permission of its
author was obtained to print it entire in the report of the Depart-
ment of Agriculture of Ontario, Canada.

The changes in membership are as follows:

December 26, 1898, members	1298	
Associates	107	
Honorary	10	
Total		1415
New members qualified during year		219
		1634
Resigned	19	
Died	7	
Dropped from roll	39	
		65

Dec. 26, 1899, members, 1430; associates, 131; honorary, 8; total 1569

The membership of the various local sections is:

Rhode Island Section	27
Cincinnati Section	67
New York Section	361
Washington Section	105
Lehigh Valley Section	19
Chicago Section	52
Nebraska Section	16
North Carolina Section	22
Columbus Section	22
North Eastern Section	232
Philadelphia Section	97
Michigan Section	35
Total	1055
Members not enrolled in any section	514
Total membership, December 26, 1899	1569
Per cent. of membership in local sections	67+
" " " " not in local sections	33—

A few additional facts regarding the local sections may be of interest. *The Rhode Island Section*, territory the State of Rhode Island, headquarters, Providence, has held 8 meetings during the year at which papers were read and discussed. *Cincinnati Section*, territory a 75-mile radius from Cincinnati, except as specified, headquarters, Cincinnati, 8 meetings with papers, net gain of membership during the year, 25. *New York Section*, territory a 50-mile radius from New York City Hall, headquarters, New York City, 10 meetings, 45 papers presented by 35 different authors, net gain in membership during the year, 64. *Washington Section*, territory, District of Columbia, State of Maryland and the State of Virginia east of the 79th meridian, headquarters, Washington, 8 regular meetings, and three special, net gain in membership, 4. This section has also 30 local associates. *Lehigh Valley Section*, territory, that portion of the Lehigh Valley included between Easton and Mauch Chunk, headquarters, Lafayette College, Easton, and Lehigh University, South Bethlehem, 2 meetings, no change in membership. *Chicago Section*, territory, Chicago and suburbs, headquarters, Chicago, 7 meetings, gain in membership, 2. *Nebraska Section*, territory, the State of Nebraska, headquarters, Lincoln, 4 meetings, no change in membership. *North Carolina Section*, territory, the State of North Carolina, headquarters, Raleigh, 2 meetings, gain in membership, 7. *Columbus Section*, territory, a 75-mile radius from Columbus, except as specified, headquarters, Columbus, monthly meetings, gain in membership, 8. *North Eastern Section*, territory, the States of Maine, New Hampshire, Vermont, and Massachusetts, headquarters, Boston, Mass., 8 meetings, gain in membership, 32. *Philadelphia Section*, organized May 17, 1899, territory, a 60-mile radius from Philadelphia, except as specified, headquarters, Philadelphia, 2 meetings. *Michigan Section*, chartered December 7, 1899, territory, the State of Michigan, headquarters, the University of Michigan, Ann Arbor.

The present constitution has come into full operation during the past year. The council, as now constituted, will number 45 during the year 1900, composed of four members *ex-officio*, 12 past presidents, 17 representatives of Local Sections, and 12

councilors at large. The number of directors is 7, all of whom are members of the council.

During the past year the Committee on Papers and Publications has been enlarged to include representatives from the various departments of chemistry, making the total membership of the committee 10, the editor being chairman.

The final report of the Committee on Coal Analysis was presented at the Columbus Meeting, last summer, and the committee was discharged. This report has been sent to the Journal for publication.

The Committee on Duty-Free Importations, having already presented a highly satisfactory report, was also discharged at the Columbus meeting.

A Committee on Patent and Related Legislation, consisting of 25 members, with Charles E. Munroe as chairman, was appointed early in the year.

An International Committee on Atomic Weights has been appointed during the year to confer with similar committees from other national organizations in order to secure cooperation on the subject entrusted to the committee. The chairman of this committee is F. W. Clarke, whose annual report upon atomic weights has appeared regularly in the columns of the Journal during the past few years.

The only new life membership during the year is that of Charles E. Munroe, of Washington. We are encouraged, however, to expect others soon. The life membership fund now established in accordance with the constitution is set aside as a permanent investment, and it is to be hoped that this fund will rapidly accumulate in the near future.

The library of the Society is substantially housed on shelves in the rooms of the Chemists' Club, 108 W. 55th St., New York City. M. T. Bogert resigned as librarian during the year and A. A. Breneman was appointed acting librarian. Professor Breneman has done a great deal of work in putting the library in condition for use of the members, and his efforts have been highly appreciated by those who understand what has been accomplished. It is to be hoped that the society will soon be able to expend upon the library whatever is necessary to keep it in good condition, and to provide for its reasonable development.

Meanwhile, it is of interest to know that the trustees of the Chemists' Club in New York have voted to defray the expenses of a card catalogue for the library.

At the Columbus Meeting committees were appointed to draw up memorials with reference to the two honorary members of the society, Sir Edward Frankland and Professor Robert Wilhelm Eberhard Bunsen, who have died during the past year. The committee on Sir Edward Frankland reports at the present meeting, but the committee on the Bunsen memorial has deferred its report in order to obtain fuller information in regard to American chemists who have been pupils of Professor Bunsen. It is hoped that at least all members of the Society who have ever been his pupils, or have had any personal acquaintance with Professor Bunsen will forward without delay to the secretary of the Society any personal reminiscences and other matters of interest, including the names and addresses of any American chemists who have ever been in any way associated with Professor Bunsen.

A message of congratulation was sent by the president and secretary of the Society to Professor J. H. van't Hoff, one of our honorary members, upon the occasion of the celebration in Rotterdam on December 22, of the twenty-fifth anniversary of Professor van't Hoff's receiving the doctor's degree.

The record of the Society during the past decade, its present flourishing condition, and the outlook for the future, are cause for congratulation to every one who has at heart its welfare and its usefulness. Ten years ago its membership was but 205; to-day it is 1569, and we believe its influence and successful work has increased with even greater rapidity. Ever since its reorganization some ten or twelve years ago its growth has been rapid and vigorous, and under its wholesome and inspiring influence the chemists of America are, year by year, brought closer together in fraternal interest.

Respectfully,

ALBERT C. HALE, *Secretary.*

REPORT OF THE TREASURER FROM MAY 1 TO DECEMBER 21, 1899.

NEW YORK, DECEMBER 21, 1899.

RECEIPTS.

Balance from treasurer, Dr. McKenna	$ 891	16
Received for dues from secretary	1175	00
Subscriptions	215	87
Received for back number		50
Received for advertising.	729	87
Received for interest, Knickerbocker Trust Co	1	35
Received for loan on special investment bond	1200	00
Received for interest on special investment bond	35	00
Received for interest on life-membership fund	36	60
	$4285	35

DISBURSEMENTS.

For publication of Journal, 7 issues	$1933	46
For reprinting January Journal	133	69
For author's reprints	133	42
For expenses, editor's office	27	54
For expenses, secretary's office (clerical)	403	83
For expenses, secretary's office (current)	197	85
For expenses, secretary's office (general)	426	15
For expenses, secretary's office, collection of dues	117	50
For expenses, library shelves	13	20
For expenses, treasurer's office	22	14
For expenses, New Haven Meeting	11	00
For expenses, general	42	49
For expenses, rebate on subscription	4	00
For advertising	1	76
For emigrant savings bank	36	60
For rebate to local sections as follows:		

Cincinnati	$ 88	33
Columbus	30	00
New York	200	00
North Eastern	30	00
Philadelphia	100	00
	$ 448	33

Balance in Knickerbocker Trust Co., Dec. 21, 1899	332	39
	$4285	35

Unpaid bills, editor's salary	$250	00
Unpaid bills, treasurer's services	150	00
Total	$400	00

A. P. HALLOCK, *Treasurer.*

Accounts examined and found correct, E. & O. E.

WM. MCMURTRIE,
J. H. WAINWRIGHT,
ELWYN WALLER,
Finance Committee.

ACTING LIBRARIAN'S REPORT FOR 1899.

NEW YORK, December 23, 1899.

To the Council of the American Chemical Society :

GENTLEMEN—The library of the Society has been in my charge, as acting librarian, since May 16th of the present year. It is now arranged in the library room of the Chemists' Club. The collection is largely made up of chemical periodicals, in sets more or less complete, but largely unbound. To put it into shape for convenient use it is imperative that much binding should be done and that the incomplete sets should be filled up. A catalogue should also be made. No money has been available for these purposes, and I hereby renew my previous suggestion to the council that an appropriation of $200 be made for binding, and in addition recommend that the sum of $500 be applied during the coming year to the purchase of missing numbers of periodicals already represented in the library.

By the action of the trustees of the Chemists' Club, recently taken, the expense of preparing a card catalogue will be assumed by the club. A printed catalogue for the use of members at a distance should be provided for by the Society. I would suggest that the council consider, as soon as possible, the question of de-

fining the plan upon which the library shall be built up. At present it has a large quantity of material which is of very remote interest to chemists, and the care of this adds materially to time and expense required in the work of the library. It seems to me that this library should be a chemical library first of all. With the means and influence of the American Chemical Society it may be made one of the best chemical libraries in the country— perhaps in time the best—but it can only fulfil its purpose by means of some reasonable system of limitation or exclusion which shall avoid the accumulation of other matter, which general libraries can much better supply. As the library is likely always to be located in one of the large cities where general library facilities are abundant, the propriety of making it strictly a library for chemists is the more apparent.

The financial affairs of the library have been reported to the treasurer of the Society, and will appear in his annual statement.

<div align="center">Very respectfully,</div>

<div align="right">A. A. BRENEMAN, *Acting Librarian*.</div>

<div align="center">REPORT OF THE EDITOR FOR 1899.</div>

To the Members of the American Chemical Society :

It is surely not necessary to announce to the world that we have in the space of seven or eight years grown into a vigorous, lusty Society. This meeting especially offers evidence of the union of the best American chemists in our effort.

It is a matter of great rejoicing to those of us who have been pulling in the traces so long, doing the best we could with material sometimes unpromising, that the best of the profession have one by one come to our aid and that we are rapidly approaching the goal.

When I became editor in 1893 there were two papers ready for publication and five numbers of the Journal in arrears. This had come to pass through the process of reorganization. Since that time progress has been steady and of late years rapid.

At the Columbus Meeting the council took what is generally considered a great step in advance in increasing the size of the Publication Committee. This increase in numbers has several advantages.

First.   Most papers may be published at once after reference to only one member particularly versed in the portion of chemistry covered by the paper.

Second.   The number of papers referred to each member is decreased, decreasing the individual burden and increasing the chance of careful consideration and wise, helpful suggestion.

The committee intends to use material of value from every available source.   The effort will be made to weed out redundancies and to pay some attention to the manner of statement as well as to the matter contained.   It is our intention to offer only helpful criticism to the authors of papers with a desire for their cooperation in making the pages of the Journal a proper reflection of American progress in chemistry.

Two factors seem to be needed in this work : First, cordial cooperation from contributors to the Journal ; and second, proper financial support.   Both of these seem now assured.

An index to the first twenty volumes has been prepared and will shortly be published.

At this meeting of the council the editor will propose that a committee be constituted to investigate the question of what is the best book-paper for our use and to make recommendations concerning it.

In conclusion it may not be uninteresting to summarize here what has been done since I became editor.   In 1893 the Journal contained 98 papers, with a total of 720 pages.   In 1894 there were 16 pages of proceedings and 152 papers, covering 891 pages, a total of 907 pages.   In 1895 there were 72 pages of proceedings and 145 papers, covering 1010 pages, a total of 1082 pages. In 1896 we printed 126 pages of proceedings and 142 papers, covering 1124 pages, a total of 1250 pages.   In 1897 we printed, for the first time, a Review of American Chemical Research, 210 pages, proceedings 66 pages, and 124 papers, covering 966 pages, a total of 1242 pages.   In 1898 there were 182 pages of review, 106 pages of proceedings, and 126 papers, covering 999 pages, a total of 1289 pages.   This year we have printed 157 pages of review, 106 pages of proceedings, and 135 papers, covering 1187 pages, a total of 1450 pages.   During this period the edition has been increased from 750 to 2000 copies.   Of the November, 1899, issue, 1679 copies were sent out.   With the steady

increase of membership, which still keeps up, we shall probably have to still further increase the edition for 1901.

EDWARD HART, *Editor.*

REPORT OF THE COMMITTEE ON MEMBERSHIP.

To the Council of the American Chemical Society :

GENTLEMEN—Your Committee on Membership desires to report one of the most successful years in the history of the Society in the acquisition of members. The total number of nominations passed upon by the committee is 256, of which 226 are active, and 30 associate members. While two special influences may be noted, namely, the formation of a Michigan Section and the meeting now in progress in New Haven, it will nevertheless be seen from the following statement how natural, steady, and healthful has been our growth.

January, 46 ; February, 21 ; March, 30 ; April, 11 ; May, 20 ; June, 8 ; July, 4 ; August, 7 ; September, 11 ; October, 23 ; November, 34 ; December, 41.

While congratulating the Society on this prosperity, your committee feels that our efforts must in no way be relaxed as with a still larger membership, a wider scope can be given the Society and a greater usefulness to the Journal.

It has been suggested by several of the most active members at work in securing the interest of students in the work of the Society that the interests of all would be better subserved if students elected to associate membership should be advanced to full membership on the simple forwarding of their credentials of graduation. This would obviate the necessity of a new form being made out and passed through the routine of the committee.

Respectfully submitted,

CHARLES A. DOREMUS, *Chairman,*
A. A. BRENEMAN,
PETER T. AUSTEN.

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

December 1, 1899.

To the American Chemical Society :

Your Committee on international action relative to a uniform system of atomic weights begs to submit the following report of progress :

It has communicated with several foreign organizations: namely, the German, English, and Belgian chemical societies. At our request the English society has appointed a committee upon the subject; and in the chemical section of the British Association, at its recent meeting, the proposition for international action was somewhat discussed, a letter from the chairman of this committee being the basis for discussion. The attitude of the English organizations towards the plan for an international conference, is altogether favorable; that of the other societies is not definitely stated. The Belgian society has formally adopted the table of atomic weights issued last year by the German committee, and several other local organizations in Europe have done the same thing.

In our conferences various questions have arisen as to nomenclature, standards and methods of stating results. On these subjects no present action is recommended, partly because of differences of opinion, and partly because final action could be of weight only when agreed to by all leading chemical societies. For us to act now would savor too much of forestalling the desired international decisions. Neither do we recommend the adoption of any specific tables of atomic weights, for three such tables, which are fairly in agreement, are now proposed; and a fourth table would only lead to confusion. The tables of the German committee, of Clarke, and of Richards are all more or less in use; and although the differences between them are minor, their reconciliation should be effected by the larger body of experts which will probably be formed.

The Congress of Chemists which will meet in Paris in July next, seems to afford the best opportunity for a general discussion of the subject; not only as to the values to be adopted, but also as to the best method for clearing up outstanding uncertainties in our constants. Your committee therefore offer the following recommendations:

First, that the officers of the above-mentioned Congress be requested to invite a joint meeting of all international committees upon atomic weights, to be held during the Congress in July, 1900, and under its auspices.

Second, that the joint committee so formed shall have power to add to its membership.

Third, that the American Chemical Society shall invite the cooperation of other organizations in the United States. The American Academy of Arts and Sciences has already appointed a committee, consisting of Professors T. W. Richards, Wolcott Gibbs, and Ira Remsen, a committee with which we should act in harmonious relations.

<div align="center">Very respectfully,</div>

<div align="right">F. W. CLARKE, Chairman.</div>
<div align="right">J. W. MALLET.</div>
<div align="right">EDWARD W. MORLEY.</div>
<div align="right">THEO. W. RICHARDS.</div>
<div align="right">EDGAR F. SMITH.</div>

<div align="center">REPORT OF COMMITTEE ON PRIESTLEY MEDAL.</div>

<div align="center">WASHINGTON, D. C., December 16, 1899.</div>

Dr. Edward W. Morley, President American Chemical Society:

SIR :—Your committee, to which was referred the consideration of the motion, " That on the twenty-fifth anniversary of the establishment of the Society, a medal be given to that chemist who, in the opinion of the council, has made the most valuable contribution to chemical knowledge during the current year, and further, that the medal be called the ' Priestley Medal '," begs to report that it deems it inadvisable for the society to found a medal from funds obtained from dues of members, since in its judgment medals and prize funds should be independently acquired for the specific purposes named by the donors.

Your committee recommends that some recognition be made of the twenty-fifth anniversary of the founding of the Society, which will occur on April 6, 1901, and it suggests that provision be made for a special memorial address, and that a statement of what the Society has accomplished to that date be published, and issued to all the chemists in America.

<div align="center">Respectfully submitted,</div>

<div align="right">CHARLES E. MUNROE, Chairman.,</div>
<div align="right">J. W. MALLET,</div>
<div align="right">ALBERT B. PRESCOTT.</div>
<div align="right">Committee.</div>

BOARD OF DIRECTORS.

MINUTES OF THE MEETING OF THE BOARD OF DIRECTORS,
DECEMBER 28, 1899.

At the close of the meeting of the council in the Kent Chemical Laboratory, New Haven, President Morley called the Board of Directors to order. There were present Messrs. Morley, Hale, Hallock, Dudley, and McMurtrie.

Upon motion duly seconded and carried, the directors authorized the appropriation of the funds recommended by the various motions approved by the council at the session just closed.

There being no further business, the board then adjourned.

ALBERT C. HALE, *Secretary*.

COUNCIL.

MINUTES OF THE COUNCIL OF THE AMERICAN CHEMICAL
SOCIETY, DECEMBER 28, 1899.

The council was called to order at 2.10 P.M., in the Kent Chemical Laboratory, New Haven, Conn., President Edward W. Morley in the chair.

There were present Messrs. Morley, McMurtrie, Hale, Hart, Catlin, Wiley, Hillebrand, Johnson, Clarke, Marshall, Gooch, Smith, Sabin, Love, Hallock, Alden, Long, Munroe, Talbot, Dudley, Prescott, and Wells.

The minutes of the council, as recorded in the secretary's book up to date, were approved.

It was voted that all nominees for membership, up to the close of this meeting, be considered as acted upon by the council, and the secretary shall declare them elected whenever all the other requirements of the constitution, in regard to them as nominees, shall have been met.

Dr. Hart reported progress for the "Committee on Exchanges" and Dr. Dudley for the "Committee on Abstracts and Reviews."

A report was presented by the committee appointed to consider a plan for celebrating the twenty-fifth anniversary of the founding of the Society, by awarding a medal for the "most valuable contribution to chemical knowledge," etc. The committee reported adversely upon the question of the medal but recommended a plan for celebrating the twenty-fifth anniversary of the

Society. The report was accepted and its recommendations adopted.

It was voted that hereafter, at the annual meeting of the council, nominations shall be made for the ensuing year, to fill the various offices and committees, the incumbents and members of which are to be elected by the council, in accordance with the constitution.

Upon motion of Professor Clarke, the following was adopted :

Resolved, That the officers of the council for the coming year shall be nominated by ballot ; if for any office a nominee shall receive a majority of the votes cast, he shall be declared to be elected to said office ; in other cases, the names of the three nominees having the highest number of votes shall be referred to the council for further balloting.

It was voted that publication in the Journal of the Society, of any action of the council, shall be considered as sufficient notice to the councilors that such action has been taken.

It was voted that the next general meeting of the society shall be held on Monday and Tuesday, June 25 and 26, in connection with the meeting of Section C of the A. A. A. S.

The report of the Finance Committee was presented and the following recommendations were adopted :

1. At the general annual meeting, each officer shall submit a schedule comprising his estimated expenses, in detail, for the coming year.

2. After all such estimates shall have been submitted, the council shall prepare a budget of expenses and the directors shall, upon the recommendation of the council, apportion the funds of the Society, or so much thereof as may be necessary, in accordance therewith.

3. All officers of the Society, who shall in any manner collect or receive moneys from any source, shall transmit the same monthly to the treasurer with a statement of the source or sources from which such receipts are collected.

4. All disbursements on account of the Society shall be made only by the treasurer upon vouchers duly approved by the Finance Committee, after having been checked by the officer by whose account the disbursement is made ; and the treasurer shall, in keeping his accounts, charge every disbursement to

some one of the several appropriations made by the directors in accordance with the preceding recommendations.

The following recommendation of the Finance Committee was referred to the various local sections of the Society for the expression of opinion thereon : " In regard to the apportionment of the Society's funds for the benefit of local sections, the Finance Committee believe, and earnestly recommend, that the following system would be preferable to the one at present in force ; *viz.*, that when the local membership of the section is below fifty (50) that section shall be entitled to draw annually an amount equivalent to one-third of the aggregate dues paid to the Society by its members. If the membership shall exceed 50 and be less than 200 the section shall be entitled to draw one-fourth ; and if it shall reach a total of 200 the section shall be entitled to draw one-fifth."

The following suggestion was referred back to the Finance Committee after a number of the councilors had expressed themselves adversely in regard to it : In regard to the general manner of conducting the business of the Society the committee are strongly of the opinion that it would be extremely desirable and would result in a very decided economy to employ for that purpose a business manager at a reasonable salary ; to turn over to him all the details connected with its administration comprising the actual keeping of all accounts, the details of correspondence, etc., etc., and to locate the Society's business at some central office.

The report of the Committee on Library Appropriations was received and placed on file, also the report and recommendations of the acting librarian.

On motion of Dr. McMurtrie it was voted that $400, or so much thereof as may be necessary, be and the same is hereby appropriated for the binding of unbound material in the library and the completion of sets, and that $100, or so much thereof as may be necessary, be and the same is hereby appropriated to pay for clerical services of the librarian.

On motion of Dr. Munroe it was voted " that it is the sense of the council that the phrase ' which shall be held in perpetuity to guarantee the future interests of such life members,' in Section 2, Article X, of the constitution, means that the income from

each life membership fee shall, during the life of the member who paid this fee, be turned into the treasury to be used in meeting the general expenses of the Society just as the annual dues of members are now used."

It was resolved that Dr. Marcus Benjamin and the editor be appointed a Committee on Portraits for the Journal. It was voted that a Committee on Paper to be used in the Journal, be appointed, consisting of three members, of which the editor shall be *ex-officio* chairman. (By subsequent vote of the Council this committee was increased to five, consisting of the following persons: Edward Hart, chairman, Henry Carmichael, A. D. Little, M. L. Griffin,and C. B. Dudley.)

It was voted that the editor be authorized to cause to be printed sample pages of the December issue, including the cover, the advertising pages, the annual table of contents, and one signature of reading matter, the whole to be used for advertising purposes.

The committee appointed to attend the Pure Food and Drug Congress held in Washington, D. C., January 8 to 20, reported that it had performed the duties assigned it and that nothing was accomplished by the Congress. The report was accepted and the committee discharged.

Upon motion by Dr. Wiley the thanks of the Society, through the council, were extended to the retiring president for the able direction of the affairs of the Society during the past year.

W. F. Hillebrand submitted the following amendments to the by-laws : Substitute for Section 17," The Journal of the Society shall not be sent to members or associates until after the receipt of their dues for the current year.

"The secretary shall have the above printed on his annual notification that dues are payable, and shall call the attention of delinquent members to it at least once every three months."

Amend Section ·20 by substituting for the first sentence the following : " The Secretary shall give written notice to the editor, immediately before the mailing of the first annual number of the Journal, of all persons in arrears, in order that the provisions of the by-laws regarding such cases may be carried into effect."

The Council then adjourned.

ALBERT C. HALE, *Secretary.*

The following named officers were elected by the Council January 30, 1900 :

Secretary—Albert C. Hale.

Editor—Edward Hart.

Treasurer—Albert P. Hallock.

Librarian—E. G. Love.

Director—Charles F. Chandler.

Members of Committee on Membership—Charles A. Doremus, A. A. Breneman, Peter T. Austen.

Members of Finance Committee—Elwyn Waller, J. Howard Wainwright.

Members of Committee on Papers and Publications—Edward Hart, Editor, *Chairman*, H. N. Stokes, W. A. Noyes, H. P. Talbot, A. A. Noyes, H. W. Wiley, Wm. McMurtrie, W. F. Hillebrand, John H. Long, and Edgar F. Smith.

In view of the fact that the number of pages in the December issue of the Journal (because of the extent of the index and the Review of American Chemical Research) unavoidably exceeded the limit of 150 pages ordered by the council, the treasurer was authorized by council to pay for the entire issue at the rates prescribed in the contract.

A Committee on Paper to be used in the Journal, consisting of three members, was authorized at the New Haven meeting of the Council. On January 30, 1900, authority was given the president to increase the number of members of this committee to five.

The Council has directed that persons who as undergraduates have been elected associates shall be declared to be members upon graduation from the chemical course of any institution of recognized standing.

NAMES PROPOSED FOR MEMBERSHIP.

Armsby, Prof. H. P., State College, Pa.

Arnott, George W. Campbell, 27 William St., N. Y. City.

Bach, August, 537 Nelson St., Chicago, Ill.

Bullard, Frank D., 245 Bradbury Block, Los Angeles, Cal.

Douglas, William, Plantation Diamond, Demerara, British Guiana.

Goodell, Geo. A., 284 St. Nicholas Ave., N. Y. City.

Hamlin, Addison, 25 5th St., Bangor, Me.

Hulett, Geo. A., 706 S. Thayer St., Ann Arbor, Mich.

Mills, James E., Chapel Hill, N. C.

Mork, Harry S., 21 Wabeno St., Roxbury, Mass.
Norris, Robert Stewart, Santa Maria, Cal.
Remington, Joseph P., 1832 Pine St., Philadelphia, Pa.,
Richards, Joseph, 1802 Catherine St., Philadelphia, Pa.
Richardson, William Derrick, 4803 Madison Ave., Chicago, Ill.
Ross, Herbert W., 1070 16th St., Oakland, Cal.
Syme, W. A., Raleigh, N. C.
Thorne, Ernest E. H., Bridgeton, Barbadoes, B. W. I.
Thurlow, Nathaniel, 55 New St., Newark, N. J.
Weld, Fred. C., Littleton, Mass.
Wolfe, J. V., Jr., Rochester, Mich.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Bates, Hugh H., 502 E. 3d St., Cincinnati, Ohio.
Berghausen, Oscar, 644 Crown St., Walnut Hills, Cincinnati, Ohio.
Black, Jesse A., Poly. Inst., Worcester, Mass.

NEW MEMBERS ELECTED JANUARY 30, 1900.

Archibald, Eben H., 109 Ellery St., Cambridge, Mass.
Ballard, J. Clarence, U. S. Expt. Station, Lafayette, Ind.
Behr, Gustave E., Jr., 1256 Massachusetts Ave., Cambridge, Mass.
Black, Otis F., 10 Avon St., Cambridge, Mass.
Bonnet, Frederic, Jr., 13 Mellen St., Cambridge, Mass.
Cohoe, Wallace P., 14 Boylston Hall, Cambridge, Mass.
Colhane, Daniel F., 58 Moore St., Cambridge, Mass.
Dailey, J. Glanding, care Carpenter Steel Co., Reading, Pa.
Davis, Robert S., 1330 12th Ave., Altoona, Pa.
Downey, James E., 10 Taylor St., Holyoke, Mass.
Earle, Richard B., 403 Craigie Hall, Cambridge, Mass.
Hale, William J., 42 Kirkland St., Cambridge, Mass.
Havens, Franke S., 9-13 Mercer St., N. Y. City.
Kittredge, Harvey G., Dayton, O.
Krebs, H. J., Wilmington, Del.
MacIntosh, Douglas, 208 E. 61st St., N. Y. City.
Sandford, Wm. E., Kewanee, Ill.
Sanger, Charles R., Chem. Lab., Harvard College, Cambridge, Mass.
Schaak, Milton F., 108 Penn St., Brooklyn, N. Y.
Williams, Simon E., Boylston Hall, Cambridge, Mass.

NEW MEMBERS ELECTED FEB. 13, 1900.

Alexander, Jerome, 502 W. 45th St., N. Y. City.
Jandrier, Edmond, Peace Dale, R. I.

ASSOCIATES ELECTED FEBRUARY 13, 1900.

Craig, Archibald G., 5516 Graham Place, Pittsburg, Pa.
Gearing, James H., 2111 Sidney St., Pittsburg, Pa.
Stifel, Walter H., 1319 Locust St., Allegheny, Pa.
Waters, Oliver G., 223 5th Ave., Pittsburg, Pa.
Wells, Allan, 213 S. St. Clair St., Pittsburg, Pa.

CHANGES OF ADDRESS.

Adgate, Matthew, care General Chem. Co., Syracuse
Works, Syracuse, N. Y.
Anderson, Duncan, Jr., 104 8th St., Roanoke, Va.
Behr, Arno, Arlington Court, Pasadena, Cal.
Burwell, A. W., 208 Superior St., Cleveland, Ohio.
Cairns, Fred. I., Anaconda, Mont.
Davis, Wm. Walley, care Va. Iron, Coal and Coke Co.,
Bristol, Va.-Tenn.
Enequist, John, 556 Greene Ave., Brooklyn, N. Y.
Escher, Paul, care Acker Process Co., Niagara Falls, N. Y.
Field, Chas., 3d, 1747 Lawrence St., Denver, Col.
Fischer, Robert, 208 Stewart Ave., Ithaca, N. Y.
Fleck, Herman, Belleville, N. J.
Foster, John, Sheffield, Ala.
Given, Arthur, 1 Plympton St., Worcester, Mass.
Hartman, Wm. E., Kalamazoo Gas Works, Spring and
Pitcher Sts., Kalamazoo, Mich.
Kelley, John H., care Tenn. Phosphate Co., Ridley,
Maury Co., Tenn.
Kelly, F. G., Chapel Hill, N. C.
Lorenz, H. W. F., Univ. of Pa., Philadelphia, Pa.
Ludlow, Gabriel, Box 344, Wilmington, N. C.
Miller, F. W., Talladega, Ala.
Miller, Hugh L., 24 Broad St., Charleston, S. C.
du Pont, P. S., The Johnson Co., Lorain, Ohio.
Schoen, Joseph, care Standard Syrup Ref. Co., 12 S. Com-
mercial St., St. Louis, Mo.
Simons, Frank D., "The Montrose Flats," 1115 9th St.,
Washington, D. C.
Small, Fritz H., care Graton & Knight Mfg. Co., Worcester,
Mass.
Smith, Frederic J., Box 46, Elizabeth, N. J.
Thorburn, A. D., Room 200, 100 State St., Chicago, Ill.
Twitchell, E., Wyoming, Ohio.

ADDRESS WANTED.

Wolff, Frank A., Jr., formerly Columbia Univ., N. Y. City.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The 72nd regular meeting was held on Friday, December 29, 1899, in the Auditorium of Hanna Hall, University of Cincinnati, with about 150 persons in attendance.

Dr. Alfred Springer presented the subject : '' A Trip through the Yellowstone Park'' beautifully illustrated by a great number of photographic lantern-slide views.

The meeting was then resumed in the Chemical Lecture Room, with 26 members present, and President Simonson in the chair. Dr. Thomas Evans made a preliminary report on ricinine. After the reading of the reports of officers for the past year, the election of officers for 1900 was held, resulting in the following ticket :

President, Thomas Evans ; *Vice-presidents,* Hannah L. Wessling, Raymond M. Hughes ; *Secretary,* Frank I. Shepherd ; *Treasurer,* Henry B. Foote ; *Executive Committee,* B. M. Pilhashy, Otto Dieckmann, Fred. Homburg ; *Representative in the Council,* Alfred Springer (elected at the November meeting).

The following chairmen of standing committees were elected :

On Papers and Publications, Frank I. Shepherd ; T. H. Norton and E. Twitchell, associate members ; *On Didactic, Physical, and Inorganic Chemistry,* T. H. Norton ; *On Organic Chemistry,* Thomas Evans ; *On Analytical Chemistry,* Wm. Simonson ; *On Medical, Physiological, and Biological Chemistry,* Wm. H. Crane ; *On Technical and Pharmaceutical Chemistry,* J. Everhard Weber.

Upon motion, the meeting adjourned.

S. WALDBOTT, *Secretary.*

PHILADELPHIA SECTION.

The meeting was called to order in the Harrison Laboratory, University of Pennsylvania, December 21, 1899, at 8.20 P.M., by the presiding officer, 35 members and visitors being present.

Prof. George F. Barker presented the paper of the evening '' Some Recent Progress in Physics.'' He called attention to the method employed to measure the wave-lengths of some extremely high-pitched notes.

He also showed the spectrum of the new gas neon which was

prepared by Prof. Dewar and samples of the newly discovered substance radium which emits rays similar to the X-rays.

The meeting adjourned at 9.50 P.M.   F. E. DODGE, *Secretary.*

WASHINGTON SECTION.

The regular meeting was held on December 14, 1899.

The first paper of the evening was read by Dr. W. D. Bigelow and was entitled " Determination of Metals in Canned Goods," by W. D. Bigelow and L. S. Munson.

After an examination of a number of the methods most commonly employed the authors gave preference to a modification of Allen's method.

The entire contents of the can are thoroughly mixed, and 75 to 100 grams taken for analysis.   Often it is found preferable to dry the entire sample, extract with petroleum ether, again dry and grind, to obtain a permanent sample.   In this case only 25 grams are employed in the determination of metals.

In either case the sample taken is treated with 4 cc. of strong sulphuric acid, 2 cc. of nitric acid, and 3 grams of magnesia. The whole is heated on a water-bath until it becomes pasty.   It is then ignited over a Bunsen burner or in a muffle-furnace until thoroughly charred, ground in a mortar, again ignited to complete combustion, nitric acid being added from time to time towards the close of the operation.   The residue is then boiled for a half hour in about 40 cc. of dilute hydrochloric acid (1 : 3), almost neutralized with sodium hydroxide, precipitated with hydrogen sulphide and filtered.   The precipitate is dried and thoroughly mixed with 1 gram each of sodium carbonate, potassium carbonate and sulphur, fused for one-half hour in a covered porcelain crucible, digested in water and filtered.

The insoluble portion contains copper and lead.   It is dissolved in nitric acid, and divided into two equal portions, in one of which the lead is precipitated as chromate and in the other copper is determined by titration with potassium cyanide.   The filtrate from the fused sulphides is acidified with acetic acid, filtered and the precipitate thoroughly washed and transferred together with the filter-paper to a solution of ferric chloride, which is heated to the boiling-point and titrated with potassium bichromate.   Zinc is precipitated as sulphide in the filtrate from

the original sulphide precipitate, after adding acetic acid and neutralizing the mineral acid with sodium hydroxide.

The second paper of the evening was read by Dr. Fireman, and was entitled: "The Action of Ammonium Chloride upon Tetra- and Pentachlorides" (preliminary communication), by P. Fireman and E. G. Portner.

The last paper of the evening was read by Mr. J. D. Tinsley and was entitled: "On the Estimation of the Water-soluble Constituents of Soils," by J. D. Tinsley and F. K. Cameron.

Dr. Seaman spoke on the size of medicine droppers found in the market. He had found them very variable, giving drops of different sizes. He showed that the size of the drop depends on the external diameter of the orifice and not on the thickness of the walls.

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The regular meeting was held on January 11, 1900. The following officers were elected for the ensuing year: *President*, Dr. H. C. Bolton; *Vice-presidents*, Mr. V. K. Chesnut and Dr. Peter Fireman; *Secretary*, Mr. William H. Krug; *Treasurer*, Mr. W. P. Cutter; *Exccutive Committee*: The above officers and Messrs. Wirt Tassin, E. E. Ewell, H. N. Stokes, F. K. Cameron, and W. F. Hillebrand.   WILLIAM H. KRUG, *Secretary*.

NEW YORK SECTION.

The regular meeting of the New York Section was held at the Chemists' Club, 108 West 55th street, on Friday evening, January 5th, Dr. C. F. McKenna, presiding.

In addition to the program announced, Prof. George F. Barker was the unexpected guest of the section. He exhibited a sample of "Radio-active Substance A"; also, some photographs made by the same on sensitized plates, which had been wrapped in three thicknesses of orange-yellow paper, and as many thicknesses of black paper over them. Prof. Barker gave a brief historical sketch of the work done on this compound, bringing the subject up to date. The room was darkened to enable the audience to observe the feeble luminosity of the substance.

The regular program was then proceeded with and the following papers were read: "Laboratory Method for the Continuous and Uniform Generation of Acetylene and its Purification," by J. A. Mathews; "Upon the Carbide of Gold," by J. A. Mathews and L. L. Watters; "On the Reactions of Alkalies with the Cellulose Nitrates," by C. W. Volney; exhibition of lantern slides illustrating "Filters for Purifying Public Water Supplies," by Allen Hazen.

DURAND WOODMAN, *Secretary.*

LEHIGH VALLEY SECTION.

A regular meeting of the Lehigh Valley Section was held at Easton, Pa., in the Chemical Laboratory of Lafayette College, on Thursday evening, January 18th. Presiding Officer Richards was in the chair and eighteen members and invited guests were present. The following papers were read : "The Action of the Weaker Organic Acids on Carbonates," by Joseph W. Richards and Norman S. Powell; read by Mr. Powell. "An Abrasion Test for Emery," by Porter W. Shimer. "Goldschmidt's New Apparatus for Cutting Crystal Models," by Joseph W. Richards. "A Method for Determining Zinc by the Use of Standard Thiosulphate Solution," by Richard K. Meade.

RICHARD K. MEADE, *Secretary.*

Proceedings.

COUNCIL.

In view of the U. S. Treasury decision 21170 relative to free importation of philosophical apparatus and preparations, which is likely to affect seriously the work of educational institutions and the laboratories of research, the council has voted that the president of the Society be authorized and directed to appoint a committee consisting of fifteen members of the Society, who shall be instructed to consider the present status of the laws and regulations governing the free importation of instruments, apparatus, and materials used in research work, and to take such action in the premises in the direction of securing such new legislation or modifications of existing laws and regulations as they may find necessary to the interests of the educational and research institutions.

The council has also voted that the president be authorized to appoint from the membership five persons to represent the Society in the Fourth Congress of Applied Chemistry, and that the sum of one hundred francs, or the equivalent thereof, be and is hereby appropriated for a subscription from the Society to the expenses of the said congress.

The following named persons have been elected by the council to the offices mentioned:

Charles F. McKenna, councilor for term expiring December, 1901.

Ernest E. Smith, director for term expiring December, 1901.

John A. Mathews, member of Finance Committee.

NAMES PROPOSED FOR MEMBERSHIP.

Carveth, Hector R., Chem. Lab., Cornell Univ., Ithaca, N. Y.
Cratty, John M., Chem. Lab., Navy Yard, Norfolk, Va.
Davies, Charles T., 1412 Perkiomen Ave., Reading, Pa.
Dunn, Willis A., 736 Fifth Ave., Helena, Mont.
Griffith, Herbert E., Galesburg, Ill.

Hooker, Samuel C., Spreckels Sugar Ref., Philadelphia, **Pa.**
McFarland, Wm. S., Barrett Mfg. Co., Philadelphia, Pa.
Mork, Harry S., 21 Wabeno St., Roxbury, Mass.
Norris, Robert S., Santa Maria, Cal.
Rosentwist, Birger G. A., Fessenden St., Jamaica Plain,
Boston, Mass.
Ross, Herbert W., 1070 16th St., Oakland, Cal.
Smith, Fred D., Missoula, Mont.
Starz, Emil, 204 N. Rodney St., Helena, Mont.
Syme, W. A., Raleigh, N. C.
Taylor, H. W., Lab. Tenn. Cotton Oil Co., Memphis, **Tenn.**
Whittier, Charles T., Provident Chem. Wks., St. Louis, **Mo.**

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Burke, Edmund, Bozeman, Mont.
Clark, Clara, Bozeman, Mont.
Cockrill, Irwin, Bozeman, Mont.
Draper, Charles W., Bozeman, Mont.
Evans, James A., 110 N. Thayer St., Ann Arbor, Mich.
Lamme, Maurice, Bozeman, Mont.
Reese, Herbert J., Bozeman, Mont.
Spragg, Frank A., Bozeman, Mont.
Wood, Jas. Leslie, Jr., Bozeman, Mont.

CHANGES OF ADDRESS.

Adams, Isaac, 1776 Massachusetts Ave., N. Cambridge, **Mass.**
Austin, N. M., 1236 Pennsylvania Ave., Allegheny, Pa.
Bassett, W. H., N. J. Zinc Co., Newark, N. J.
Baxter, Wm. T., 254 New York St., Aurora, Ill.
Beck, Oscar C., 305 S. 40th St., Philadelphia, Pa.
Becker, J. B., 1104 Douglass St., Sioux City, Iowa.
Clarke, Thomas, Birmingham, Ala.
Couch, Guy E., 631 E. Front St., Cincinnati, Ohio.
Crane, Frederic, 28 Hillside Ave., Montclair, N. J.
Gabriel, Geo. A., Box 390, Cumberland Mills, Me.
Hall, C. A., 3220 Powelton Ave., Philadelphia, Pa.
Harding, E. P., 22 Landhaus Strasse, Heidelberg, **Germany.**
Henderson, W. E., Ohio State Univ., Columbus, Ohio.
Johnson, E. S., 315 Highland Ave., Syracuse, N. Y.
Keller, Edward, P. O. Box 724, Baltimore, Md.
Kelly, F. G., care Tenn. C. I. & R. Co., Birmingham, **Ala.**
Lyng, M. H., Republic, Wash.
Mason, Francis P., 214 Monadnock Bldg., Chicago, Ill.
Miller, F. W., Talladega, Ala.
McBryde, J. B., Blacksburg, Va.
Perkins, Albert S., 75 Milton Ave., Hyde Park, Mass.

Peyton, Wm. C., Peyton Chem. Wks., Mutual Life Bldg., San Francisco, Cal.

Reese, Chas. L., N. J. Zinc Co., Newark, N. J.

Seidensticker, L. J., 178 Thornton St., Boston, Mass.

Shilstone, Herbert M., 166 St. James Place, Brooklyn, N. Y.

Smolt, F. O., 23 N. Tejou St., Colorado Springs, Col.

Sy, Albert P., 24 High St., Buffalo, N. Y.

Thomas, W. H., care Colonial Bleaching & Printing Co., St. Henry, Montreal, Can.

Torrey, Chas. A., Jr., 1015 S. 48th St., Philadelphia, Pa.

Wolff, Frank A., Jr., Columbian Univ., Washington, D. C.

Worstall, Robert A., 139 Kennard St., Cleveland, Ohio.

ADDRESSES WANTED.

Hartman, Wm. E., 843 Lafayette Ave., Detroit, Mich.

Wood, J. R., 439–441 Green St., Philadelphia, Pa.

CORRESPONDENCE.

The following is the copy of a letter received by ex-President Morley from Dr. J. H. van't Hoff, in response to the Society's cablegram :

CHARLOTTENBURG, January 27, 1900.

My Dear Colleague :

I beg you to express my feelings of thankfulness to the American Chemical Society, which gladdened and honored me by its telegraphic congratulations on my jubilee. At the same time I have to thank you and the secretary, Mr. Hale, more especially, the congratulation having your names. With my best wishes for the prosperity of your Society, I am,

Yours truly,

J. H. VAN'T HOFF.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The seventy-third regular meeting of the Cincinnati Section was held in the Chemical Lecture Room of Hanna Hall, University of Cincinnati, on Monday evening, January 15, 1900. President Evans occupied the chair. Twenty-five members were present.

Dr. Otto Dieckmann read a paper on "Researches on Methyl-benzimid-azole," which was a report on some of the author's work done under the direction of Prof. Zincke, at Marburg.

By special request Dr. Evans gave an extended résumé of the contents of his paper on "Ricinine" read by title at the December meeting.   FRANK I. SHEPHERD, *Secretary.*

NORTH EASTERN SECTION.

The regular monthly meeting of the section was held on Thursday evening, January 18th, President Little calling the meeting to order, with 63 members present.

After the transaction of business, Mr. Henry Howard presented a paper on "The Manufacture of Aluminum Sulphate by the Bayer Process," sketching the history of the alumina industry and explaining the theory and practice of the new method of manufacture.

A paper on "The Canned Foods Industry" by Mr. W. L. Underwood followed, in which was given the development of the business since its foundation in 1819, the difficulties which have been met, and how they have been overcome. In connection with this subject Mr. S. C. Prescott presented a paper on "The Preservation of Foods." This paper was illustrated by drawings and photographs of the micro-organisms which are found on, and in vegetables and other foods, and the author explained the methods by which these are destroyed. After examining the samples with which all the papers were illustrated, the meeting adjourned.

The February meeting was held on Friday evening February 16th, at the Hotel Oxford, Vice-president Elihu Thomson in the chair and 60 members present.

The first paper of the evening was presented by Mr. Thomson on "The Properties of Carbon in Their Relation to Electrical Work." The author discussed the peculiar properties of carbon on which the development of applied electricity has so largely depended, calling special attention to those properties requisite for the terminals of arc lights, for incandescent light filaments, telephone transmitters and generating machine brushes.

The next paper was by Dr. F. H. Thorp on "The Potash Industry as seen at Stassfurt." After describing the position and composition of the different strata of the Stassfurt deposit, the author explained the method of mining and preparing for

market the different potash salts which are of commercial importance.

The section considered the resolutions which have been drawn up by the Committee on Instruments of Measure relating to the establishment of a National Standards Bureau, and on motion of Dr. H. P. Talbot the following resolution was adopted.

Resolved, That the members of the Northeastern Section of the American Chemical Society heartily endorse the proposed movement to secure the establishment of a National Standards Bureau for the verification of chemical apparatus, in connection with the United States Office of Weights and Measures; and that they desire to record as their opinion that such a bureau is urgently demanded in the interests of pure and applied chemistry in the United States.

At 10.10 the meeting adjourned.

W. H. WALKER, *Secretary.*

NORTH CAROLINA SECTION.

The fourth annual meeting of the North Carolina Section was called to order in the office of the State Chemist, Raleigh, at noon, February 24, 1900, by the presiding officer, Dr. Charles Baskerville. Sixteen members and invited guests were present.

After the reports of the different committees the following was introduced and carried :

Resolved, That it is the sense of the North Carolina Section that Article X, Sec. 1, of the Constitution of the American Chemical Society be so amended that when the local membership of a section is below 50 that section shall be entitled to draw annually an amount equivalent to one-third of the aggregate dues paid to the Society by its members. If the membership shall exceed 50 and be less than 200 the section shall be entitled to draw one-fourth ; and if it shall reach a total of 200 the section shall be entitled to draw one-fifth.

A committee consisting of F. P. Venable, B. W. Kilgore, and W. A. Withers were appointed with carte-blanche to draft and forward resolutions to Congress in relation to the establishment and maintenance in connection with the Bureau of Weights and Measures, a department to graduate and verify weights and volumetric apparatus.

The following papers were read and discussed :

" Temperature for the Graduation of Volumetric Apparatus for Southern Laboratories," by B. W. Kilgore ; " On the Qual-

itative Determination of Tin, Arsenic and Antimony," by Charles Baskerville; "Radio-active Bodies," by F. P. Venable; "Composition of Commercial Chromium Sulphate," by F. P. Venable; "Variable Ammonia Results in Mixed Fertilizers Containing Either Fish Scrap, Blood, Tankage, or Nitrate of Soda," by C. B. Williams; "Chemical Economics," by Charles Baskerville.

Officers elected for the ensuing year are :

President, B. W. Kilgore ; *Vice-president*, W. J. Martin, Jr.; *Secretary and Treasurer*, C. B. Williams; *Representative in Council for 1901*, Charles Baskerville ; *Executive Committee*, B. W. Kilgore, W. J. Martin, Jr., and C. B. Williams.

There being no further business the section adjourned.

C. B. WILLIAMS, *Secretary*.

PHILADELPHIA SECTION.

The seventh meeting was called to order in the Harrison Laboratory, University of Penna., January 18, 1900, at 8.20 P.M., 13 members being present. The presiding officer being absent Dr. Mathews was elected chairman for the evening. The minutes of the last meeting were read and approved.

The recommendation of the Finance Committee of the American Chemical Society, in relation to the distribution of dues for the benefit of the local sections, was read and discussed by Messrs. Shinn, Mathews, Kebler, and others. It was moved and seconded that the recommendation of the Finance Committee be accepted. Carried.

The following papers were presented :

"A Study in Iodination" by J. F. X. Harold, in which he called attention to the fact that it appeared that nobody had studied the reaction resulting from the action of hydrogen sulphide on iodine in the presence of alcohols, such as methyl alcohol, ethyl alcohol, etc. He showed that in the presence of an excess of iodine, the nascent hydriodic acid formed, attacked the alcohols forming iodides of the alcohol radical.

Lyman F. Kebler called attention to some of the exceedingly stringent requirements of the U. S. Pharmacopoeia, such as 100 per cent. purity, the absolute exclusion of chlorides and sulphates in such products as sodium benzoate, lithium carbonate, potassium hypophosphite, etc. He thought it very desirable to

have high standards, but they should not be beyond a point reasonably attainable. Many inconsistencies were pointed out in the 1890 edition. He also discussed at some length, why the American Chemical Society should be represented by several delegates at the Decennial Pharmacopoeial Convention. This may not be feasible for the convention that convenes next May, but in view of the fact that several of the states have already passed Food and Drug Adulteration Laws, making the U. S. P. standard in cases under these laws, it seems eminently desirable that the American Chemical Society should have representatives on the 1900 U. S. Pharmacopoeial Revision Committee.

The meeting adjourned at 9.45 P.M.

F. K. DODGE, *Secretary.*

COLUMBUS SECTION.

The Columbus Section has held its regular monthly meetings, the following papers having been presented during the present collegiate year.

" Reminiscences of Bunsen," by S. A. Norton ; " Cyclic Methylene Compounds," by C. C. Howard ; " A Discussion of Werner's Hypothesis," by Wm. E. Henderson ; " The Action of α-Acylphenylhydrazines on Chlorquinones," by Wm. McPherson ; " The Detection of Blood," by A. M. Bleile ; " The Midwinter Meeting of the American Chemical Society," by Wm. McPherson.

The following officers have been elected for the year :

President, H. A. Weber ; *Secretary,* Wm. McPherson ; *Treasurer,* W. E. Henderson ; *Committee on Membership,* G. B. Kauffman, A. M. Bleile ; *Member of Council,* Wm. McPherson.

WILLIAM McPHERSON, *Secretary.*

NEW YORK SECTION.

The regular meeting of the New York Section was held in the assembly room of the Chemists' Club, 108 West 55th Street, on Friday evening, February 9th, at 8.30 P.M., Dr. C. F. McKenna presiding. There were about 50 members present.

Resolutions relative to a National Standards Bureau, forwarded by the chairman of the Committee on Standards of Instruments of Measure of the American Chemical Society, were read and, on motion, approved.

The following papers were then read : " The Technical Analysis of Rope and Twine," by Durand Woodman ; "A New Synthesis in the Phen-miazin Series," by M. T. Bogert and August Gotthelf ; "On the History of Photo-chemical Improvements, with Experiments," by Maximilian Toch.

A motion was made and seconded empowering the chair to appoint a committee to arrange for a meeting to be devoted to "Laboratory Apparatus and Products."

The meeting adjourned to meet March 9th.

DURAND WOODMAN, *Secretary*

Proceedings.

The twenty-first general meeting of the American Chemical Society will be held in New York City, Monday and Tuesday, June 25 and 26, 1900. Members desiring to present papers are urged to send titles and abstracts as soon as possible to the secretary, Albert C. Hale, 551 Putnam Ave., Brooklyn, N. Y.

COUNCIL.

The amendments to the by-laws offered by Dr. Hillebrand were not adopted, a majority of the council voting against them.

NAMES PROPOSED FOR MEMBERSHIP.

Berkeley, Wm. N., San Juan, Puerto Rico.
Bertelli, Riccardo, 20 W. 16th St., N. Y. City.
Blake, Lucien I., Univ. of Kas., Lawrence, Kas.
Colley, Bernard T., care C. K. C. S. & R. Co., Argentine, Kas.
Davis, Charles B., 518 Manhattan Ave., N. Y. City.
Ebaugh, W. Clarence., 3741 Lancaster Ave., Philadelphia, Pa.
Ginder, W. H. H., Vandergrift, Pa.
Hatchett, Roger H., Argentine, Kas.
Hill, Edwin A., Patent Office, Washington, D. C.
Hofmann, Ottokar, Argentine, Kas.
Irwin, Edward B., 714 W. 11th St., Kansas City, Mo.
Jessup, A. E., Office of Supervising Architect, Treasury Dept., Washington, D. C.
Johnson, Flowmoy C., 714 Union St., New Orleans, La.
Koelle, Carl, Argentine, Kas.
Moechel, Jean Robert, 710 Wyandotte St., Kansas City, Mo.
Neilson, Thomas, Tucson, Ariz.
Neish, Arthur C., Columbia Univ., N. Y. City.
Peters, Fredus N., Central High School, Kansas City, Mo.
Rudinck, Paul F. A., 3701 S. Lincoln St., Chicago, Ill.
Sloane, T. O. Coner, 39 Wall St., N. Y. City.
Smither, F. W., 36 Cole Bldg., Nashville, Tenn.
Torrey, Henry A., 75 S. Prospect St., Burlington, Vt.
Whipple, Geo. C., Flatbush Ave. & Eastern Parkway, Brooklyn, N. Y.
Whitten, W. H., Jr., Westport High School, Kansas City, Mo.
Zeizler, John Clayton, Torpedo Station, Newport, R. I.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Harriman, Norman F., Ann Arbor, Mich.
Wellard, H. H., 520 E. Ann St., Ann Arbor, Mich.

NEW MEMBERS ELECTED MARCH 9, 1900.

Armsby, Prof. H. P., State College, Pa.
Arnott, Geo. W. Campbell, 27 William St., N. Y. City.
Bach, August, 537 Nelson St., Chicago, Ill.
Bullard, Frank D., 245 Bradbury Block, Los Angeles, Cal.
Cuadrado, Gaston A., Calle de la Habana, 112, Habana, Cuba.
Douglas, William, Plantation Diamond, Demerara, British Guiana.
Gardunio, Jesur, Aguascalientes, Mexico.
Goodell, Geo. A., 284 St. Nicholas Ave., N. Y. City.
Hamlin, Addison, 25 5th St., Bangor, Me.
Herger, Charles G., 11 Putnam St., Buffalo, N. Y.
Hulett, George A., 706 S. Thayer St., Ann Arbor, Mich.
Lihme, C. B., care of Ill. Zinc Co., Peru, Ill.
Mills, James E., Chapel Hill, N. C.
Mork, Harry S., 21 Wabeno St., Roxbury, Mass.
Norris, Robert S., Santa Maria, Cal.
Remington, Joseph P., 1832 Pine St., Philadelphia.
Richards, Joseph, 1802 Catherine St., Philadelphia.
Richardson, Wm. D., 4803 Madison Ave., Chicago, Ill.
Ross, Herbert W., 1070 16th St., Oakland, Cal.
Syme, W. A., Raleigh, N. C.
Thorne, Ernest E. H., Bridgetown, Barbadoes, B. W. I.
Thurlow, Nathaniel, 55 New St., Newark, N. J.
Weld, Fred C., Littleton, Mass.
Wolf, Ernst, 214 E. 82nd St., N. Y. City.
Wolfe, J. V., Jr., Rochester, Mich.

ASSOCIATES ELECTED MARCH 9, 1900.

Bates, Hugh H., 502 E. 3rd St., Cincinnati, O.
Berghausen, Oscar, 644 Crown St., Walnut Hills, Cincinnati, O.
Block, Jesse A., Polytechnic Institute, Worcester, Mass.

CHANGES OF ADDRESS.

Affelder, Oscar I., care Pittsburg Gas & Coke Co., Otto, Pa.
Best, Otto, 16 Mastic Terrace, Alameda, Cal.
Busby, Fred E., Mass. Inst. Tech., Boston, Mass.
Chamberlin, W. E., 127 Pearl St., N. Y. City.
Couch, Guy E., Hartwell, Hamilton Co., Ohio.
Dodge, F. E., care Barrett Mfg. Co., Tucker & Bermuda Sts., Frankford, Pa.
Hanks, A. Abbott, 531 California St., San Francisco, Cal.
Hartman, Wm. E., Kalamazoo Gas Co., Kalamazoo, Mich.
Hough, George J., 2235 Sheridan Rd., Evanston, Ill.
Jones, A. B., Lock Box 741, Pittsburg, Pa.
Kelley, J. H., 315 N. Vine St., Nashville, Tenn.

Lichtenstein, A. F., 67 Elmwood Ave., N. Adams, Mass.

Martin, M. A., U. S. Mint, San Francisco, Cal.

Parmelee, C. W., care N. Y. & Boston Dyewood Co., 55 Beekman St., N. Y. City.

Richardson, Clifford, N. Y. Testing Lab., L. I. City, N. Y.

Skinner, Hervey J., care Moro Phillips Chem. Co., Camden, N. J.

Tucker, S. A., Havemeyer Hall, Columbia Univ., N. Y. City.

Walker, P. H., care Ala. Consolidated C. & I. Co., Gadsden, Ala.

Watkins, W. H., 87 Poplar St., Roslindale, Mass.

MEETINGS OF THE SECTIONS.

PHILADELPHIA SECTION.

The eighth meeting was called to order February 15th, at 8.25 P.M. in the Harrison Laboratory, University of Pennsylvania, February 15th, 20 members being present, the presiding officer was in the chair. The minutes of the last meeting were read and approved.

A letter from the chairman of the Committee on " A National Standardizing Bureau" of the American Chemical Society, was read ; also a set of resolutions, which after some discussion were adopted as read.

A motion was made that the section meet promptly at 8 o'clock in the future. Seconded and carried.

Mr. George Auchy presented the paper of the evening : " Remarks on Some Methods of Determining Carbon in Steel." The paper was discussed by Messrs. Meeker, MacFarland, Sargent, Job, and Jayne.

There being no further business the meeting adjourned at 10 P.M.   F. E. DODGE, *Secretary*.

ORGANIZATION OF MICHIGAN SECTION.

The first meeting of the Michigan Section of the American Chemical Society was held at the house of Professor Prescott in Ann Arbor, on Friday, February 28th, at four in the afternoon. Of the 42 members of the section in the State, 26 had promised to be present, but the heavy snow on that day blocked railroad traffic to such an extent that most of the members not resident in Ann Arbor who attempted to come, spent the day i- trains

stalled in snow-drifts. The meeting was called to order by Professor Prescott, with 16 members of the section present, and Dr. Wiley, of Washington, as an invited guest. Professor R. C. Kedzie of the Agricultural College was elected temporary chairman. Dr. Prescott gave a short statement of the movement he had started leading to the granting of a charter to the Michigan Section with territory covering the state of Michigan, and headquarters at the University of Michigan. Dr. Wiley was asked for remarks and responded with his congratulations on the formation of the new section, and an account of the methods of the Washington Section. The by-laws recommended by the Committee of Arrangements were adopted and the following officers elected for the year 1900 :

Presiding Officer, Professor A. B. Prescott, Ann Arbor ; *Secretary and Treasurer*, Alfred H. White, Ann Arbor ; *Member of Council*, Professor Paul C. Freer, Ann Arbor ; *Elective Members of Executive Committee*, A. F. Shattuck, Chemist Solvay Process Co., Detroit ; F. S. Kedzie, Professor, Agricultural College; J. V. Wolfe, Jr., Chemist Detroit Sugar Co., Rochester.

At the close of the business meeting, the members were entertained at dinner by Professor Prescott, and later listened to an illustrated lecture by Professor Freer on '' Liquid Air.'' Many of the members also attended the sessions of the State Farmers' Institute on the following day when Dr. Wiley and others spoke on various questions pertaining to the beet-sugar industry.

ALFRED H. WHITE, *Secretary.*

CHICAGO SECTION.

Two meetings of the Chicago Section were held during February at the Union Restaurant, 111 Randolph St.

On the 8th, Mr. D. H. Trowbridge gave a very interesting paper on the '' Manufacture and Chemistry of Beet Sugar.''

On the 28th, Prof. W. O. Atwater, of Wesleyan University, who was the guest of the section gave an informal talk on the respiration calorimeter and its results.

F. B. DAINS, *Secretary.*

Proceedings.

BOARD OF DIRECTORS.

A meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York City, March 21, 1900. There were present Messrs. McMurtrie, Hale, Hallock, Doremus, and Smith.

The meeting was called to order by President McMurtrie at 8:20 P.M. The minutes of the previous meeting were approved, as recorded in the secretary's book. Upon motion of Dr. Doremus the following schedule of prices for the Journal was adopted, and all previous schedules of prices inconsistent therewith were repealed.

For volumes of either 10 or 12 numbers:

	To members.	To non-members.
Current volume	$5.00	$6.00
" numbers	0.50	0.60
Back volumes	3.00	6.00
" numbers	0.30	0.60

For volumes of less than 10 numbers:

	To members.	To non-members.
Volumes	$3.00	$6.00

Numbers at proportionate rates. Discount to dealers, 15 per cent. on prices to non-members.

· The librarian was directed to have prepared 1000 copies of a circular letter setting forth the above prices.

In order to economize space in the library, the librarian was authorized to prepare for binding any unbound material belonging to the library.

He was also authorized to exchange or sell, at his discretion, any duplicate material; and further, to publish in the advertising pages of the Journal a list of the numbers missing from the files in the library.

The treasurer was authorized to pay the note of the Society which falls due March 27.

The board then adjourned to meet in the same place, Friday, March 23, at 3 P.M.

An adjourned meeting of the Board of Directors of the American Chemical Society was held at the Chemists' Club, 108 W. 55th St., New York, March 23, 1900. There were present Messrs. McMurtrie, Hale, Hallock, Dudley, Doremus, and Smith.

The meeting was called to order by President McMurtrie at 8:40 P.M. The minutes of the meeting held March 21, were read and approved.

Upon motion of Dr. Doremus the schedule of prices for the Journal adopted at the last meeting was reconsidered and was amended so as to read as follows:

For volumes of either 10 or 12 numbers:

	To members.	To non-members.
Current volume	$5.00	$6.00
" numbers	0.50	0.60
Back volumes	4.00	6.00
" numbers	0.40	0.60

For volumes of less than 10 numbers:

	To members.	To non-members.
Volumes	$4.00	$6.00

Numbers at proportionate rates. Discount to dealers, 15 per cent. on prices to non-members.

It was voted that the librarian be requested to furnish to the Board of Directors a survey of the sets of the Journal now the property of the Society that the same may be scheduled for sale.

The following preamble and resolutions were unanimously adopted:

"WHEREAS, in a letter to the secretary of the Society, dated February 6, 1900, formal notice of the termination of the contract for printing the Journal of the Society was given by the Chemical Publishing Company, and

WHEREAS, the Chemical Publishing Company, in a letter to the secretary, dated February 20, 1900, proposed to continue for a period of 6 months, from May to October, inclusive, to publish the Journal in consideration of a bonus of ten dollars ($10) a month above the price fixed by the contract,

Be it Resolved, that the Board of Directors, by and with the consent of the council, hereby accepts the notice of the termination of the contract, and agrees to pay to the said Chemical Publishing Company the bonus of ten dollars ($10) per month above

the price fixed by the contract, in consideration of the temporary continuation, in accordance with all the terms of the said contract of the publication of the Journal from May to October 1900, inclusive.

The minutes of the meeting were read and approved. The board then adjourned.

COUNCIL.

The following report and recommendations have been received from the Committee on Standards for Instruments of Measure, and have been approved by the council.

January 10, 1900.

To the Council of the American Chemical Society.

GENTLEMEN : We, the undersigned, members of the Committee on Standards for Instruments of Measure of the American Chemical Society, have considered the resolutions transmitted herewith and beg to ask your favorable consideration and action upon them, in accordance with the following motion passed by the Society at the recent New Haven meeting:

"Moved to refer the suggestions and resolutions of Mr. Ewell to the Committee on Standards for Instruments of Measure for consideration and report to the council which is requested to take action in the matter; and, further, that the Committee on Standards for Instruments of Measure be empowered to increase its number for the purpose of considering this subject."

We recommend further, that these resolutions be printed with the signatures of the officers and councilors of the Society, and in sufficient number so that one thousand copies will be available for the use of this committee after copies have been transmitted by the secretary of the Society to the persons or bodies designated in the resolutions and to as many additional persons or bodies as your wisdom may suggest.

Your committee, named in the motion quoted above and as enlarged in accordance therewith, beg to so interpret that motion that the powers therein granted will be fully utilized, and the duties therein imposed will be duly executed, by each member of the committee constituting himself a sub-committee of one to place a copy of the resolutions in the hands of every person whose interest and efforts he believes will aid the movement; and by persuading him, by personal letters or by conversation when possible, to seek to impress the importance of our request upon as many as possible of the members of the two houses of Congress and of the appropriate committees thereof.

We also ask that the proper committees and officers of the Society be empowered and directed to honor bills for expenditures

for postage incurred in the execution of this plan by the ten members constituting this committee.

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Respectfully,

E. E. EWELL, *Chairman*,
G. E. BARTON,
C. E. LINEBARGER,
H. P. TALBOT,
LOUIS A. FISCHER,
F. W. CLARKE,
C. B. DUDLEY,
E. W. MORLEY,
C. E. MUNROE,
H. W. WILEY.

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Committee on Standards for Instruments of Measure of the American Chemical Society.

RESOLUTIONS RELATIVE TO A NATIONAL STANDARDS BUREAU.

WHEREAS, in the conduct of exact chemical and physical investigations, the use of apparatus of guaranteed accuracy is a necessity which is recognized by all physicists and chemists ; and

WHEREAS, in foreign countries, notably in Germany and England, such guarantee is furnished by standardizing bureaus under the control of their respective governments ; and

WHEREAS, at present the U. S. Office of Standard Weights and Measures does not possess appliances necessary for the verification of as wide a range of apparatus in kind and form as seems essential, nor the working force requisite to comply with legitimate demands for the verification and stamping of chemical and physical apparatus, thus compelling the importation of foreign-made apparatus when such official certification is desired ; and,

WHEREAS, this state of affairs is not only unsatisfactory to all chemists, but also works injustice to our manufacturers of thermometers, hydrometers, volumetric apparatus and other chemical measuring instruments who can not supply the proper certification with such apparatus ; therefore be it

Resolved, that the congress of the United States be urged to establish a National Standards Bureau in connection with the U. S. Office of Standard Weights and Measures which shall provide adequate facilities for making such verification of chemical measuring apparatus and for stamping the same, as are provided by foreign governments for similar work.

Resolved further, that a copy of the foregoing be forwarded to the Secretary of the Treasury, under whose control the present office of Standard Weights and Measures comes ; to the Super-

intendent of the U. S. Coast and Geodetic Survey; to the President of the U. S. Senate; to the Speaker of the U. S. House of Representatives; to the Chairman and members of the Committee on Coinage, Weights and Measures; and, to the presiding officers of the various sections of this Society and to the presiding officers of other scientific bodies likely to be interested, with a request for the cooperation of those organizations in our efforts to secure for the U. S. Office of Standard Weights and Measures ample facilities, in point of apparatus and working force, to enable that office to comply with the requests for the verification of measuring instruments that may be made by American scientific workers.

> E. E. EWELL, *Chairman*,
> G. E. BARTON,
> C. E. LINEBARGER,
> H. P. TALBOT,
> LOUIS A. FISCHER,
> F. W. CLARKE,
> C. B. DUDLEY,
> E. W. MORLEY,
> C. E. MUNROE,
> H. W. WILEY.

Committee on Standards for Instruments of Measure of the American Chemical Society.

REFERENCES TO SOME RECENT LITERATURE ON THIS SUBJECT.

"Volumetric Apparatus." By G. E. Barton. *J. Am. Chem. Soc.*, 20, 731-739 (1898).

"On the Facilities for Standardizing Chemical Apparatus Afforded by Foreign Governments and Our Own." By Louis A. Fischer. *J. Am. Chem. Soc.*, 20, 912-927 (1898).

"A Brief History of the Movement for Increasing the Accuracy and for Improving the Construction of Chemical Measuring Instruments." By Ervin E. Ewell. *J. Am. Chem. Soc.*, 21, 527-550 (1899).

"Maasanalytische Studien." By Dr. Julius Wagner. (A Book Review.) By H. P. Talbot. *J. Am. Chem. Soc.*, 21, 551-555 (1899).

"On the Limits of Accuracy in Technical Analysis." By J. Grossman. *J. Soc. Chem. Ind.*, 18, 977-981 (1899).

"The Regulations of the Physikalisch-Technische Reichsanstalt Relative to Thermometers." Translated by C. E. Linebarger. *J. Am. Chem. Soc.*, 22, 121 (1900).

NAMES PROPOSED FOR MEMBERSHIP.

Ackerman, Franz W., 54 Livingston St., Brooklyn, N. Y.
Ansbacher, Louis A., 4 Murray St., N. Y. City.
Braun, F. W., 501-505 N. Main St., Los Angeles, Cal.

Emery, A. L., Palo Alto, Cal.
Frazee, F. H., 416 Concord Ave., Detroit, Mich.
Gibbon, R. Fitz, 77 John St., N. Y. City.
Hartley, Kenneth, Kansas City, Kansas.
Hartford, James, 100 William St., N. Y. City.
Hess, Henry W., 1829 Summit Ave., Toledo, O.
Hummel, John A., State Capitol, St. Paul, Minn.
Landis, Edward K., 4025 Spruce St., Philadelphia.
Neumeister, E. J., Alma Sugar Co., Alma, Mich.
Nikaido, Yasajuro, 2375 O St., Lincoln, Nebr.
Russell, Herman, 721 E. Ann St., Ann Arbor, Mich.
Schnierwind, F., Ph.D., United Coke and Gas Co., 36 Wall St., N. Y.
Soper, George A., 251 W. 93d St., N. Y. City.
Van Riper, George B., Rutherford, N. J.
Veitch, Alexander, Clifton, Ariz.

NAMES PROPOSED FOR ASSOCIATE MEMBERSHIP.

Eccles, David C., 191 Dean St., Brooklyn, N. Y.
Kiehn, John F., 3631 S. Winchester Ave., Chicago, Ill.
Stierlin, E., 1110 Queen City Ave., Cincinnati, O.

NEW MEMBERS ELECTED APRIL 28, 1900.

Berkeley, Wm. N., San Juan, Puerto Rico.
Bertelli, Riccardo, 20 W. 16th St., N. Y. City.
Blake, Lucien I., Univ. of Kansas, Lawrence, Kas.
Colley, Bernard T., C. K. C. S. & R. Co., Argentine, Kas.
Davis, Charles B., 518 Manhattan Ave., N. Y. City.
Ebaugh, W. Clarence, 3741 Lancaster Ave., Philadelphia.
Ginder, W. H. H., Vandergrift, Pa.
Hatchett, Roger H., Argentine, Kas.
Hill, Edwin A., Patent Office, Washington, D. C.
Hofmann, Ottokar, Argentine, Kas.
Irwin, Edward B., 714 W. 11th St., Kansas City, Mo.
Jessup, A. E., Office of Surpervising Architect, Treasury Dept., Washington, D. C.
Koelle, Carl, Argentine, Kas.
Moechel, Jean R., Ph.D., 710 Wyandotte St., Kansas City, Mo.
Neilson, Thomas, Tucson, Ariz.
Neish, Arthur C., Columbia University, N. Y. City.
Peters, Fredus N., Central High School, Kansas City, Mo.
Rudinck, Paul F. A., 3701 S. Lincoln St., Chicago.
Sloane, T. O'Conor, 39 Wall St., N. Y. City.
Smither, F. W., 36 Cole Building, Nashville, Tenn.
Torrey, Henry A., 75 S. Prospect St., Burlington, Vt.

Whipple, George C., Flatbush Ave. and Eastern Parkway, Brooklyn, N. Y.

Whitten, W. H., Jr., Westport High School, Kansas City, Mo.

Ziegler, John C., U. S. Torpedo Station, Newport, R. I.

ASSOCIATES ELECTED APRIL 28, 1900.

Harriman, Norman F., Ann Arbor, Mich.

Willard, H. H., 520 E. Ann St., Ann Arbor, Mich.

CHANGES OF ADDRESS.

Belden, A. W., Birmingham Cement Co., Ensley, Ala.

Bloomfield, L..M., Valencia via Catacamas Olancho, Honduras, C. A., via New Orleans.

Cluff, Clarence B., 6608 Stewart Ave., Chicago, Ill.

Granja, Rafael, care The Palen Co., Kingston, N. Y.

Haslwanter, Charles, 904 Flushing Ave., Brooklyn, N. Y.

Hayes-Campbell, J., 514 E. 6th St., Newport, Ky.

Kenan, Wm. R., Jr., care Trader's Paper Co., Lockport, N.Y.

Kirchgasser, W. C., 74 and 76 Laight St., N. Y. City.

Loeser, R. M., care First Nat. Bank, El Paso, Texas.

Luschka, Otto, care Seamon Chemical Laboratory and Assay Office, El Paso, Texas.

Magruder, E. W., Dept. of Agr., Richmond, Va.

Nelson, E. K., 4526 Oakenwald Ave., Chicago, Ill.

Power, F. B., The Wellcome Research Laboratories, 6 King St., Snow Hill, E. C., England.

Smith, H. E., 29 31st Street, Milwaukee, Wis.

Thatcher, R. W., Agr. Expt. Sta., Lincoln, Nebr.

Thurnauer, Gustav, Aurora Metal Co., Aurora, Ill.

Wrampelmeier, T. J., 320 California St., San Francisco, Cal.

Yeaton, Arthur C., Westbrook Sem., Portland, Me.

Zimmele, H. B., 53 South Washington Square, New York City.

MEETINGS OF THE SECTIONS.

MICHIGAN SECTION.

The Michigan Section met on Friday evening, April 27, in the parlors of the Normandie Hotel, Detroit, with 57 members and visitors in attendance. Before the meeting there was an informal dinner at which 26 were present. The following papers were presented :

" Filtration of Drinking Water." By A. F. Shattuck.

" Theory of Hardening of Steel." By E. D. Campbell.

"Distillation of Amalgams and Purification of Mercury."
By Geo. A. Hulett.

The paper announced by Charles C. Sherrard was, at his request, postponed till the next meeting.

ALFRED H. WHITE, *Secretary.*

NEW YORK SECTION.

The March meeting of the New York Section was held at the Chemists' Club, on Friday evening, March 9th, Dr. C. F. McKenna presiding.

The annual meeting of the Society at large, it was announced, would be held in New York in June in conjunction with the meeting of the Association for the Advancement of Science, and on motion it was voted that the Executive Committee be authorized to prepare for the reception of the American Chemical Society in June, and to add to their number as may be necessary.

The following papers were read :

" Normal Chlorine Map of Long Island." By Messrs. G. C. Whipple and D. T. Jackson.

" A New Industrial Process for the Separation of Oxygen, Nitrogen, and Carbon Dioxide from the Atmosphere at Extraordinarily Small Cost." By Prof. Raoul Pictet.

After a vote of thanks to Prof. Pictet the meeting adjourned.

The April meeting of the New York Section of the American Chemical Society, was held on Friday evening, April 6th, at the Chemists' Club, 108 West Fifty-fifth Street. Dr. C. F. McKenna presided, and the following papers were read :

" A Method of Obtaining Nucleic Acid." By Dr. P. A. Levene.

" Analysis of a Saline Deposit from Southern Nevada." By Ralph W. Bailey.

" Notes on the Ferrocyanide Titration of Zinc." By Dr. E. H. Miller and E. J. Hall.

Special announcement was made of an extra meeting to be held on May 2d for the exhibition of novel forms of apparatus, products, etc., and that the meeting would be in the nature of a reception, to which the ladies and friends of the members would be invited. The Section on this occasion will be the guest of the Chemists' Club.

An invitation to attend the next meeting of the New York Section of the Society of Chemical Industry, on the occasion of the presentation of a paper on "Petroleum and its Products," by Dr. C. F. Newberry, signed by Dr. Parker, was then read, after which the meeting adjourned.   DURAND WOODMAN, *Secretary*.

CINCINNATI SECTION.

The 74th regular meeting of the Cincinnati Section was held in the Chemical Lecture Room, Hanna Hall, University of Cincinnati, on Thursday evening, February 15, 1900.   Prof. R. M. Hughes occupied the chair. ' 32 members and visitors were present.

A communication from the Chairman of the Committee on Standards of Measure, of the American Chemical Society, was referred to a committee consisting of the president and secretary, with power to act.

The paper of the evening, "Expert Evidence," was presented by Dr. Alfred Springer.

The 75th regular meeting of the Cincinnati Section was held on Thursday evening, March 15th, at the usual place of meeting in Hanna Hall.   Dr. Evans presided, and 22 members and visitors were in attendance.

The Committee on a National Standards Bureau reported that it had adopted the resolutions read at the February meeting and had forwarded copies to the officials mentioned in the communication from Mr. E. E. Ewell.

Mr. Lucien Fogetti addressed the section on the subject, "Fractional Distillation in Vacuo, with a New Form of Receiver." The discussion which followed was quite generally-participated in.   Following this Mr. Fogetti gave a very interesting account of Dr. Squibb's plant and process for the manufacture of ether and absolute alcohol.

The 76th regular meeting of the Cincinnati Section was held on Saturday evening, April 14th, in the Chemical Lecture Room in Hanna Hall, with Dr. Evans in the chair.   Twenty-nine members and visitors were present.

Mr. Robert W. Hochstetter presented the paper of the evening, "Indigo."   The methods now used in India for cultivating

the plant and preparing the crude indigo of commerce were described. The more important methods of making synthetic indigo were discussed briefly. Methods of analysis were touched upon, and the paper was concluded by an interesting account of the ways in which indigo is used in dyeing, calico printing, and as a pigment. The paper was well illustrated by specimens of natural and artificial indigo and its products and by materials dyed and printed. FRANK I. SHEPHERD, *Secretary.*

WASHINGTON SECTION.

The 116th regular meeting was held Thursday, February 8, 1900.

The following program was presented :

" The Adulteration of the Arsenical Insecticides," by J. K. Haywood.

" Uncompounded Chemicals under the War Revenue Act (with exhibition of specimens)," by C. A. Crampton and D. Simmons.

" The Relation of the Chemical Society to the Municipality," by Wirt Tassin.

" The Genesis of Hardpan," by F. K. Cameron.

The 117th regular meeting was held Thursday, March 8, 1900.

The program was devoted to a symposium on iron and steel, as follows :

Iron : The raw materials ; chemistry of iron-ore smelting ; cast iron ; properties of iron.

Steel : The raw materials ; converting methods ; the mill ; castings, forgings, and plates ; special steels.

The participants were Messrs. Dewey and Tassin.

The regular meeting was held April 12, 1900.

The first paper was read by Mr. J. K. Haywood, and was entitled " The Analysis of the Arsenical Insecticides." The paper consisted of a comparative study of various methods proposed for the analysis of these preparations.

The second paper of the evening, which was presented by Dr. H. C. Bolton, and entitled " A Claim for Priority," was read by the Secretary.

"The Journal of the American Chemical Society for March, 1900, contains a paper by Joseph W. Richards and Norman S.

Powell, entitled "Substitutes for Hydrochloric Acid in Testing Carbonates;" the authors find that potassium acid sulphate, oxalic acid, citric acid, and tartaric acid can be used in testing carbonates, producing effervescence more or less actively, and they give a table of results. The authors make no reference to previous work on the same lines, and this prompts me to make the claim that about twenty years ago I anticipated all their observations and published the results in periodicals accessible to every one.

"Between 1877 and 1882 I published three memoirs under the title 'Application of Organic Acids to the Examination of Minerals,' in which I showed the action of these acids on 200 mineral species, including carbonates, sulphides, oxides, silicates, and many others. I pointed out the usefulness of citric acid as a substitute for hydrochloric acid in the laboratory and in the field, and showed that by means of it certain minerals could be readily distinguished.

"These papers were printed in whole or in part in the following journals : *Chemical News*, Vols. 35, 36, 43, and 47 ; *Annals N. Y. Acad. Sciences*, Vols. I and II ; *Proceedings American Assoc. Adv. Science*, Vol. 47 ; *Reports Brit. Assoc. Adv. Science*, Vol. 50 ; *Mineralogical Mag.*, Vol. IV ; *Ber. d. chem. Ges.*, Vol. XIII ; and abstracts appeared in many other journals. Moreover the use of citric acid in testing minerals was adopted by teachers in more than one scientific school, the use of potassium acid sulphate having been known long before. Finally Nason's edition of Elderhorst's 'Manual of Qualitative Blowpipe Analysis' (1881) gives a whole chapter to my method.

" It is gratifying to note that the results obtained by Richards and Powell agree well with mine. Coincidences of independent thought often occur, but in publishing a research some acknowledgment of previous work is generally made ; had the authors made even a slight examination of familiar literature they would have found that their field of study had been thoroughly traversed."

The third paper was read by Dr. Cameron and was entitled "The Estimation of the Carbonates and Bicarbonates of the Alkalies," by F. K. Cameron and L. J. Briggs.

The last paper was read by Dr. Cameron and was entitled "The Solubility of Calcium Sulphate in Solutions of Other Salts," by F. K. Cameron and F. D. Gardner.

Mr. Chestnut exhibited specimens of plants used by the Indians in California, to stupefy fish which they use for food.

An adjourned meeting was held at Hopkins Hall, Johns Hopkins University, Baltimore, Md., on April 21, 1900.

Dr. Remsen welcomed the Society and explained that the Chemical Department of the University is now undergoing repairs after damage by fire. He gave an interesting account of the work in progress under his direction in the university laboratory.

The first paper of the evening was read by Dr. Simon and was entitled "A Storage Vessel for Solid Carbon Dioxide." The author exhibited an improved vessel, which he had designed, and which is giving universal satisfaction in the transportation of such materials as solid carbon dioxide and liquid air. In connection with the vessel, he exhibited some solid carbon dioxide which had been placed in it.the day before and showed that there had been very little loss.

Professor Morse read a paper on the preparation of permanganic acid, in which he discussed various methods and showed that the electrolytic method had been most satisfactory. He described, in detail, the apparatus used for carrying out this method.

Dr. Bolton presented a paper entitled "An Experimental Study of Radio-active Substances." The paper was illustrated with photographs taken with radium light.

The last paper of the evening was read by Dr. F. W. Clarke and was entitled "The Action of Ammonium Chloride on Certain Silicates," by F. W. Clarke and George Steiger.

"A brief outline of the method of decomposition of some zeolites, by heating with ammonium chloride in a sealed tube, was first given.

"It was shown by the experiments that two of the formulas, hitherto given, to scolecite, natrolite, and prehnite, must be abandoned.

"Scolecite and natrolite give almost identical ammonium compounds, calcium having been replaced in the one case and sodium in the other. They also show these two zeolites to be probably salts of orthotrisilicic acid.

"In the case of prehnite the results were quite different, two experiments giving only 0.17 per cent. in one case and 0.22 per cent. in the other of ammonium in the product formed by their treatment. This different action shows that prehnite can no longer be classed with the former two.

"In the case of pectolite the results were so irregular that definite conclusions could not be drawn from the facts at hand. Some figures were given and a formula suggested."

W. H. KRUG, *Secretary*.

Proceedings.

COUNCIL.

The following resolutions have been approved by council :

WHEREAS, the laws of the several states controlling food adulterations are largely ineffective because of the interference of interstate commerce laws, and can be made effective only through national legislation,

AND WHEREAS, by bills now pending in the congress of the United States and particularly by bills numbered H. R. 9677 and Senate 2426, it is proposed to establish in the United States Department of Agriculture a bureau of chemistry, the director of which shall, under the direction of the secretary of agriculture, be charged with the chemical investigation of the foods produced and consumed throughout the country.

Therefore be it resolved by the Council of the American Chemical Society that the congress of the United States be, and is hereby, urged to promptly enact into law the said bills, namely H. R. 9677, and Senate 2426, and provide adequate facilities for effective prosecution of the provisions of the said bills.

Resolved, further, that a copy of this resolution be forwarded to the president of the United States Senate ; to the speaker of the House of Representatives ; to the chairman of the Committees on Agriculture and on Commerce and Manufactures of the Senate of the United States; to the chairman of the Committee on Interstate Commerce of the House of Representatives ; to the secretary of agriculture, who shall be charged with the enforcement of the provisions of said bills, and to the presiding officers of the various sections of the Society, urging their cooperation in the movement to secure the establishment of the bureau of chemistry, which shall be charged with the scientific and chemical work required in the enforcement of the provisions of the said bills.

NAMES PROPOSED FOR MEMBERSHIP.

Allen, Richard F., Hart Park, West New Brighton, Staten Id., N. Y.

Berolzheimer, Daniel D., 175 E. 79th St., N. Y. City.

Hancock, Wm. J., Erasmus Hall, High School, Brooklyn, N. Y.

Logan, Lily, Howardsville, Va.

Lohmann, Herman J., 90 Monticello Ave., Jersey City, N. J.

Norton, Mrs. Alice P., 47 Hancock St., Auburndale, Mass.

Richards, Alfred N., 437 W. 59th St., N. Y. City.

Stockwell, C. F., Bassett, Nebr.

Sundstrom, Carl, care Solvay Process Co., Detroit, Mich.

Sundstrom, Karl J., Trenton, Wayne Co., Mich.

Taylor, Thomas M., Oberlin, Ohio.

Torrey, Joseph, Jr., 8 Avon St., Cambridge, Mass.

Waddell, John, School of Mines, Kingston, Ont.

NAME PROPOSED FOR ASSOCIATE MEMBERSHIP.

Pretzfeld, Charles J., 1211 Madison Ave., N. Y. City.

NEW MEMBERS ELECTED JUNE 12, 1900.

Ackerman, Franz W., 54 Livingston St., Brooklyn, N. Y.

Ansbacher, Louis A., 4 Murray St., N. Y. City.

Emery, A. L., Palo Alto, Cal.

Frazee, F. H., 416 Concord Ave., Detroit, Mich.

Hartford, James, 100 William St., N. Y. City.

Hartley, Kenneth, Kansas City, Kans.

Hess, Henry W., 1829 Summit Ave., Toledo, O.

Hummel, John A., State Capitol, St. Paul, Minn.

Landis, Edward K., 4025 Spruce St., Philadelphia.

Mather, Henry A., care Verde Queen Copper Co., Jerome, Ariz.

Neumeister, E. J., Alma Sugar Co., Alma, Mich.

Nikaido, Yasajuro, 2375 O St., Lincoln, Nebr.

Russell, Herman, 721 E. Ann St., Ann Arbor, Mich.

Schnierwind, F., United Coke and Gas Co., 36 Wall St., N. Y. City.

Soper, George A., 251 W. 93rd St., N. Y. City.

Van Riper, George B., Rutherford, N. J.

ASSOCIATES ELECTED JUNE 12, 1900.

Eccles, David C., 191 Dean St., Brooklyn, N. Y.

Kiehn, John F., 3631 S. Winchester Ave., Chicago, Ill.

Stierlin, E., 1110 Queen City Ave., Cincinnati, O.

CHANGES OF ADDRESS.

Ashley, Harrison E., 947 Acushnet Ave., New Bedford, Mass.
Bevier, Miss Isabel, Plymouth, Ohio.
Brewer, Chas. E., Wake Forest, N. C.
Clark, Clara, 201 N. Jackson St., Butte, Mont.
Dailey, J. Glanding, 327 Wharton St., Philadelphia, Pa.
Fosdick, E. H., 1505 S. Grand Ave., Los Angeles, Cal.
Jackson, Daniel D., 179 Sixth Ave., Brooklyn, N. Y.
Johnson, Treat B., 57 Otis St., E. Cambridge, Boston, Mass.
Labonde, Dr. Leon, 3601 S. Hower St., Los Angeles, Cal.
McIlhiney, P. C., 145 E. 23d St., N. Y. City.
Perkins, T. S., care California Tartar Co., 318 Front St., San Francisco, Cal.
Phalen, Wm. C., 13 Sadler St., Gloucester, Mass.
Phillips, Wm. D., 128 Pearl St., N. Y. City.
Richardson, Clifford, care N. Y. Testing Lab., Long Island City, N. Y.
Schüpphaus, Robert C., 174 Broadway, N. Y. City.
Skinner, Hewey J., care General Chem. Co., Moro Phillips Works, Camden, N. J.
Tuschka, Otto, care Seamon Lab., El Paso, Texas.
Willard, H. H., Union City, Mich.
Willey, Ogden G., Box 179, Berwyn, Ill.

MEETINGS OF THE SECTIONS.

CHICAGO SECTION.

The 34th regular meeting of the Chicago Section was held at the Union Restaurant, May 11, 1900.

Prof. W. A. Noyes, of the Rose Polytechnic Institute, gave a paper on the constitution of camphor, showing how the problem had been attacked and the evidence for the formula now assigned.

Dr. J. H. Long was elected member of the council from the Chicago Section.   F. B. DAINS, *Secretary.*

NEW YORK SECTION.

The May meeting was held on the 12th, at the Chemists' Club, as usual, Dr. C. F. McKenna presiding. The following papers were read:

C. W. Volney: " New Extraction Apparatus."

C. W. Volney: " Artifical Musk."

P. A. Levene: " Modern Researches on the Chemistry of the Proteid Molecule."

J. A. Mathews: "Cobalticyanides of Bismuth."

Dr. Volney's artificial musk was exhibited and caused considerable discussion. It is said to be a compound belonging to the paraffin series, and therefore is a distinct departure from the idea that an artificial perfume must contain the "benzol ring." No analysis was given nor particulars of the method of preparation, these being reserved for a future communication. Asked whether his musk is composed of a saturated or unsaturated paraffin compound, Dr. Volney said that it is saturated. Dr. Schweitzer said that so far as he knew, it had never been claimed that an aromatic group was necessary in the synthetic musks. Dr. Stearns claims that nitrated bodies do not smell of true musk. Different persons, he said, are differently affected by the true musk odor, and many are incapable of deciding that an imitation is a good representative of the true flavor. In this way many substances were called artificial musk which would not pass even an arbitrary set of tests. It is not yet known what the essential element of true musk is, or whether it is preexistent, or is formed by a slow chemical change in the constituents of musk material. Baur has examined musk to determine whether nitrated bodies were present, but found none.

Dr. Levene's paper was an interesting review of the work which has been done and the views which have been held during the past two years on the chemistry of the protein compounds and the classifications of their constituents. In regard to the sulphur in their composition, he said it evidently existed in two forms or conditions of combination, one molecule being separable as hydrogen sulphide, the other remaining.

Dr. J. A. Mathews described an investigation of the cobalticyanides of bismuth designed to develop a process for separation of bismuth in analytical work — for instance, in the analysis of pig and refined lead. The conditions under which such an analysis is carried out were found, however, to prevent the complete precipitation of bismuth as cobalticyanide, and as yet he had not been able to make the practical application of the study of these salts which had been hoped for.

The meeting was addressed by Prof. Rising, of California, who said that much interest was manifested by the chemists of the Pacific coast in becoming members of the American Chemical

Society, and an application for a charter would soon be made.

Dr. McMurtrie, president of the Society, was present, and, invited to take the chair, said that in view of the approaching general meeting it was necessary that each member should bring out whatever subject he had in readiness for publication in time to have its title announced on the program. All such titles should be transmitted to the general secretary, A. C. Hale, 551 Putnam Ave., Brooklyn, N. Y., as early as practicable, to facilitate the preparation of the program and to enable the committee to arrange sufficient time for the sessions. Dr. Doremus announced the full list of sections, and ground covered thereby, in the congress of chemists to be held at Paris in July—also that titles of papers to be presented there should be forwarded not later than June 1.

The chairman referred to the special exhibition-reception meeting held on the 2nd inst. in the Assembly Room of the club, and suggested a vote of thanks to those who had assisted in making it a success. On motion, a vote of thanks was seconded and carried unanimously: to Dr. Elwyn Waller for the handsome roses sent from his greenhouses to decorate the tables; to the firms who made special exhibits of apparatus, minerals, and chemical products; and to Dr. E. E. Smith and his committee for their arduous labor in arranging the details of catalogue, printing, etc.

The June meeting of the New York Section of the American Chemical Society was held on the 8th inst. at the Chemists' Club. The retiring chairman, Dr. Chas. F. McKenna, invited the president of the Society, Dr. William McMurtrie, to preside. An address was made by Dr. McKenna on the "Advancement in the Study of the Properties of the Metals," and on the "Present and Future of the New York Section of the American Chemical Society."

The election of officers for the ensuing year resulted as follows: *Chairman*, Dr. C. A. Doremus; *Secretary and Treasurer*, Durand Woodman; *Executive Committee*, C. F. McKenna, M. T. Bogert, and P. C. McIlhiney.

The following papers were then read:

"Comparison of Iodine and Bromine Figures of Various Fatty Oils," by H. T. Vulté and Lily Logan.

"The Chemistry of Materials used in Perfumery and Kindred Arts," by T. C. Stearns.

"Rapid Method for Separation of Cadmium, Bismuth, etc., from Zinc and Manganese," by Geo. C. Stone.

"On the Oxidation of Platinum," by Dr. R. C. Hall.

A motion was made and seconded that a fund should be raised for a prize for the best paper read before the Society during each season. This was in pursuance of a suggestion made by the chairman in his address.

Notice was given of the general meeting of the American Chemical Society, to be held in the latter part of the month, after which the Section adjourned.

DURAND WOODMAN, *Secretary.*

PROCEEDINGS.

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